VOLUME 36 APRIL 1958 NUMBER 4

Canadian Journal of Chemistry

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OTTAWA CANADA

CANADIAN JOURNAL OF CHEMISTRY

(Formerly Section B, Canadian Journal of Research)

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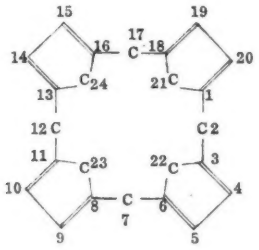
Canadian Journal of Chemistry, Vol. 36, 1958.

The drawing on page 371 should be replaced by the one appearing below.



QUATERENE NUCLEUS

Canadian Journal of Chemistry

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOLUME 36 APRIL 1958 NUMBER 4

SYNTHESIS OF 4-AMINOBUTYRIC ACID AND 2,4-DIAMINOBUTYRIC ACID FROM BUTYROLACTONE[1,2]

GUY TALBOT, ROGER GAUDRY, AND LOUIS BERLINGUET

ABSTRACT

The ring opening of γ-butyrolactone with 1 mole of potassium phthalimide and the hydrolysis of the intermediate product gave 4-aminobutyric acid with an excellent yield. The condensation of 1 mole of potassium phthalimide with 2-bromo-4-butyrolactone gave a 2-phthalimidolactone which can also be opened by treatment with a second molecule of potassium phthalimide. This diphthalimido acid when hydrolyzed gave, with an excellent yield, 2,4-diaminobutyric acid dihydrochloride.

INTRODUCTION

4-Aminobutyric acid has long been considered as a metabolic by-product of bacteria and yeast (1, 2, 3, 4). Recently it has been isolated from proteins (5), from plants (6), and from brain tissues (7). Now we know that it is a catabolic product of glutamic acid (8, 9) and that the reaction is reversible (10).

Several methods are available for its synthesis, which are classified in four groups:

(*a*) Oxidation of piperylurethan or sparteine (11, 12).

(*b*) Condensation of potassium phthalimide or of potassium cyanide with halogenated intermediates (13, 14, 15, 16).

(*c*) Reduction of succinimide or 3-cyanopropionic acid or succinonitrile (17, 18, 19, 20, 21, 22).

(*d*) Chemical or enzymatic degradation of glutamic acid or glutarimide (23, 24, 25, 26).

Even then, the abundant supply of 4-aminobutyric acid is somewhat limited because of the nonavailability of the starting products and the four or five steps required for the synthesis.

Since γ-butyrolactone is readily available, a new synthesis starting from the lactone was considered. Bornstein and his collaborators (27) and Paris, Gaudry, and Berlinguet (28) have clearly shown that phthalide can be opened by potassium phthalimide and γ-butyrolactone can be opened by potassium cyanide.

The γ-butyrolactone ring was opened with a 73% yield by reaction with potassium phthalimide in boiling dimethylformamide.

The intermediate compound was then hydrolyzed with hydrochloric acid and the free amino acid was obtained and characterized after the usual treatment with silver car-

[1]*Manuscript received December 5, 1957.*
Contribution from the Department of Biochemistry, School of Medicine, Laval University, Quebec, Que.
[2]*Paper presented before the Division of Chemistry at the 24th Meeting of the Association Canadienne-Française pour l'Avancement des Sciences (A.C.F.A.S.), Montreal, November 4, 1956.*

bonate. The yield of 4-aminobutyric acid was 68%. It was also identified by paper chromatography. The R_f values in phenol–water and pyridine–water systems are respectively 0.76 and 0.19.

Another interesting amino acid, namely 2,4-diaminobutyric acid, was synthesized using a somewhat similar pathway from γ-butyrolactone.

This naturally occurring diamino acid has been found recently in several antibiotic polypeptides (29, 30, 31, 32). The known methods of synthesis are classified in three main groups:

(*a*) Synthesis involving a phthalimido aldehyde (33).

(*b*) Synthesis involving the Hofmann degradation of glutamic acid (34, 35, 36, 37, 38) or the Curtius and Schmidt reactions (39, 40, 41).

(*c*) Synthesis from ethyl acrylate and diazomethane (42).

The last method is by far the best even if it makes use of diazomethane and high-pressure hydrogenation.

Since Livak and his collaborators (43) have brominated very easily γ-butyrolactone, this halogenated lactone was treated with one molecule of potassium phthalimide in boiling dimethylformamide. The 2-phthalimidobutyrolactone thus obtained was opened by treatment with a second molecule of potassium phthalimide.

The total yield of 3,4-diphthalimidobutyric acid from the bromolactone was 73%. This insoluble intermediate when hydrolyzed with concentrated hydrochloric acid gave an 80% yield of the 2,4-diaminobutyric acid dihydrochloride. The over-all yield from the bromolactone was nearly 60%.

The diamino acid was characterized by paper chromatography and paper electrophoresis. R_f values in phenol–water and pyridine–water systems were respectively 0.16 and 0.04. Being a diamino acid, it migrated toward the cathode in a buffer solution of pH 8.6.

EXPERIMENTAL[3]

4-Phthalimidobutyric Acid

Potassium phthalimide (18.5 g., 0.1 mole) was added to 4-butyrolactone (10.0 g., 0.116 mole) in 50 ml. of dimethylformamide. After it was boiled for 12 hours, the mixture was poured onto ice to which had been added 30 ml. of glacial acetic acid. The solid obtained was filtered and recrystallized from water and ethanol. Yield: 17.1 g. (73%), m.p. 117°–118° (Lit. m.p. 117°–118° (44)). Anal. Calc. for $C_{12}H_{11}O_4N$: N, 6.01. Found: N, 6.09.

4-Aminobutyric Acid

4-Phthalimidobutyric acid (5.0 g., 0.021 mole) was dissolved in 100 ml. of dilute hydrochloric acid (1:1). The solution was refluxed during 5 hours, after which it was cooled. The phthalic acid was filtered and the filtrate was evaporated to dryness *in vacuo*. The residue consisted of 4-aminobutyric acid hydrochloride, which was very hygroscopic. It was treated as usual with silver carbonate, hydrogen sulphide, and charcoal. Yield: 1.5 g. (68%), m.p. 195°–196° (Lit. m.p. 196° (12)). Anal. Calc. for $C_4H_9O_2N$: N, 13.57. Found: N, 13.33.

2-Phthalimido-4-butyrolactone

Potassium phthalimide (55 g., 0.297 mole) was added to a solution of 150 ml. of dimethylformamide and 2-bromo-4-butyrolactone (43) (50 g., 0.303 mole). The well-mixed solution was heated at 100° during 12 hours, after which it was poured onto ice.

[3]*Melting points are uncorrected.*

The precipitate was collected by filtration and it was recrystallized from acetone–water. Yield: 59 g. (86%), m.p. 160°–162°. Anal. Calc. for $C_{12}H_9O_4N$: N, 6.06. Found: N, 6.15.

By acid hydrolysis, the hydrochloride of 2-amino-4-butyrolactone was obtained. It gave a yellow color when treated with ninhydrin and its R_f value in a water–pyridine system was 0.75.

2,4-Diphthalimidobutyric Acid

Potassium phthalimide (10.0 g., 0.054 mole) was added to a solution of 30 ml. of dimethylformamide and 2-phthalimido-4-butyrolactone (11.56 g., 0.05 mole). The solution was heated to reflux during 7 hours. It was then poured onto ice to which 20 ml. of glacial acetic acid had been added. The precipitate was collected by filtration. Yield: 16.0 g. (85%). It can be recrystallized from acetic acid. M.p. 177°–179°. Anal. Calc. for $C_{20}H_{14}O_6N_2$: N, 7.40. Found: N, 7.27.

2,4-Diaminobutyric Acid Dihydrochloride

2,4-Diphthalimidobutyric acid (2.0 g.) was suspended in 50 ml. of dilute hydrochloric acid (1:1). The mixture was refluxed during 12 hours, after which it was cooled. The phthalic acid was collected by filtration, and the filtrate was evaporated to dryness *in vacuo*. The residue was recrystallized from a mixture of hydrochloric acid and glacial acetic acid. Yield: 0.8 g. (79%), m.p. 206° (Lit. m.p. 202°–205° (45)). Anal. Calc. for $C_4H_{10}O_2N_2 \cdot 2HCl$: Cl, 37.1; N, 14.65. Found: Cl, 36.9; N, 14.50.

ACKNOWLEDGMENTS

The authors are indebted to the National Research Council of Canada for Research Fellowships awarded to one of them (G.T.).

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ARSENATES OF THE TRANSITION METALS

THE ARSENATES OF COBALT AND NICKEL[1]

J. B. TAYLOR[2] AND R. D. HEYDING

ABSTRACT

Complex oxides occurring in the systems CoO/As_2O_5 and NiO/As_2O_5 have been studied using Debye–Sherrer diagrams. The compounds were prepared either by high-temperature reaction of the oxides and subsequent pyrolysis of the products or by aqueous precipitation of arsenates followed by thermal dehydration.

The existence of compounds having metal oxide to arsenic pentoxide ratios of 1:1, 2:1, and 3:1 has been clearly demonstrated and the thermal stabilities of each *in vacuo* and in air have been studied. Corresponding compounds in the cobalt and nickel series are isostructural and unit-cell dimensions have been determined. The compounds with a 2:1 ratio could not be isolated readily although their existence is indisputable and tentative figures for the unit-cell dimensions have been obtained.

Another compound, probably with a metal oxide to arsenic pentoxide ratio of 6:1, has been observed during the pyrolysis of the 3:1 compounds. Apparently the cobalt and nickel compounds are isostructural and represent the only phase existing between the 3:1 compounds and the metal oxides.

INTRODUCTION

Continuing an investigation into the chemistry of cobalt speiss and its behavior on roasting in air we have sought to prepare and examine the so-called arsenates of cobalt and nickel which occur in the composition range between $M^{II}O.As_2O_5$ and $M^{II}O$. Previous compounds reported were in many cases hydrates and have been called meta-, pyro-, and ortho-arsenates in the usual manner. We prefer to regard the compounds which we have studied as complex oxides and accordingly will refer to them in terms of their metal oxide to arsenic pentoxide ratios.

Both cobalt and nickel occur naturally as arsenates in the form of erythrite and annabergite respectively. These compounds are of the type $3M^{II}O.As_2O_5.8H_2O$ and have been classified crystallographically as monoclinic (space group $C2/m$), having unit-cell dimensions of $a = 10.056$ Å, $b = 13.340$ Å, $c = 4.730$ Å, $\beta = 102°0'$ for the cobalt compound, and $a = 10.015$ Å, $b = 13.284$ Å, $c = 4.698$ Å, $\beta = 102°14'$ for the nickel compound (1). The structures undoubtedly contain arsenic tetrahedrally co-ordinated with oxygen (2). These compounds have been prepared synthetically together with numerous other hydrated arsenates. The latter were of little interest as far as the present work was concerned since their structures have not been established. In general it may be said that these arsenates have metal oxide to arsenic pentoxide ratios of 0.5:1, 1:1, 2:1, 2.5:1, 3:1, 4:1, and 5:1. They were usually prepared by one of two methods: either the reaction of metal, metal oxide, or carbonate with acid at atmospheric or high pressure (3); or the precipitation of the arsenate by addition of metal ion to arsenate ion (4).

Anhydrous complex oxides of nickel have been prepared by Guérin and Masson (5) by dehydration of a hydrated arsenate, $NiO.2As_2O_5.5H_2O$, at an elevated temperature under vacuum. They report that the product $NiO.2As_2O_5$ can be pyrolyzed *in vacuo* to give $NiO.As_2O_5$, $2NiO.As_2O_5$, and $3NiO.As_2O_5$ at 550°, 650°, and 750° C. respectively.

An alternative method of making the complex oxides involves high-temperature reaction of the metal oxide $M^{II}O$ with As_2O_5 mixed in the desired proportions. Thus

[1]*Manuscript received December 11, 1957.*
Contribution from the Division of Applied Chemistry, National Research Council, Ottawa, Canada.
Issued as N.R.C. No. 4632.
[2]*N.R.C. Postdoctorate Fellow.*

$CoO.As_2O_5$ and the isomorphous calcium, strontium, cadmium, mercury, and lead compounds have been prepared (6) as well as $CoO.Sb_2O_5$, $NiO.Sb_2O_5$ (7), and several trivalent antimony and arsenic compounds (8). The so-called 'cobalt meta-arsenate' $CoO.As_2O_5$ is reported to be hexagonal (6) (space group $P312$) with unit-cell dimensions: $a = 4.766$ Å, $c = 4.493$ Å. The structure is well established, being the same as $PbO.Sb_2O_5$ (9), and contains arsenic in octahedral co-ordination with oxygen, which appears to be an exception to the generally accepted fourfold co-ordination of arsenic. Comparison of this type of structure with that of $FePO_4$ (10) reveals a considerable difference between phosphorus and arsenic in the compounds as the structural chemistry of the former is based on PO_4 tetrahedra and is probably best compared with the SiO_4 tetrahedra in silicates.

Some crystallographic data have been reported for the 1 : 1 pentavalent antimony compounds of iron, cobalt, and nickel (7) and these have been found to be isostructural, with a trirutile structure $P4/mnm$. The cell dimensions of the cobalt compound are: $a = 4.64$ Å, $c = 9.25$ Å and of the nickel analogue: $a = 4.63$ Å, $c = 9.18$ Å.

MATERIALS

The arsenic pentoxide used was Mallinckrodt 'A.R.' containing 0.05% trivalent arsenic and 0.02% lead.

The nickel oxide, cobalt oxide, and cobalt sponge were obtained from Johnson, Matthey & Co. The nickel oxide contained 5 p.p.m. of iron and no cobalt. The cobalt oxide contained 2 p.p.m. of iron and was sold as Co_3O_4 but analyzed $CoO_{1.103}$. The cobalt sponge which was finally used in the preparation of cobalt monoxide contained 5 p.p.m. of iron and no nickel.

Cobalt Oxide, CoO

The CoO was prepared by thermal decomposition of the basic carbonate under vacuum as this method proved more rapid than ignition of the Johnson, Matthey oxide. Cobalt sponge was dissolved in hot 6 : 1 nitric acid and from this solution the basic carbonate was precipitated by addition of potassium bicarbonate solution. The carbonate was decomposed to CoO by ignition in a continuously pumped vacuum system at 1040° C. for about 2 hours. The product was analyzed for cobalt and its X-ray powder diagram compared with standards.

ANALYSIS FOR COBALT, NICKEL, AND ARSENIC

Nickel was analyzed using the dimethyl glyoxime reagent and weighing as $NiC_8H_{14}O_4N_4$ after drying at 110° C. The most satisfactory method for cobalt analysis was reduction in hydrogen at 950° C. Arsenic was determined by precipitation as silver arsenate and subsequent titration of the silver with thiocyanate. Samples which contained nickel and arsenic or cobalt and arsenic in admixture were first treated to obtain a separation of the components, and the resulting solutions estimated as above. The arsenate hydrates could be dissolved in dilute nitric acid and the metal separated by slow addition of dilute sodium hydroxide solution. Samples of the complex oxides were insoluble in mineral acids and were fused with Na_2CO_3/KNO_3 (2 : 1) fusion mixture. The soluble arsenate was then readily leached out and the residue containing the metal taken up by a pyrosulphate fusion.

EXPERIMENTAL

To investigate the formation of compounds of the type $xM^{II}O.As_2O_5$ by direct reaction of the oxides at a high temperature a series of nickel oxide – arsenic pentoxide mixtures

with values of x from 1 to 3 were made and sealed under vacuum in quartz ampoules. Other mixtures were also prepared containing cobalt monoxide and arsenic pentoxide in 1 : 1 admixture. The ampoules were heated in furnaces carefully maintained at 500° C., 650° C., and 800° C. for periods of up to 9 days. In all cases attack of the quartz by the As_2O_5 took place and in the samples at 800° C. this weakened the quartz to the point that several of the ampoules exploded. Reaction between the oxides occurred in all cases, resulting in a yellow or green product in the nickel experiments and a purple product for the cobalt compounds.

Several cobalt monoxide – arsenic pentoxide 1 : 1 mixtures were made taking great care to exclude as much moisture as possible. The arsenic pentoxide for this series of experiments was dried at 400° C. for 30 hours under vacuum and all operations prior to sealing the ampoules were performed in a dry box. After heating for 5 days at 460° C. no reaction had occurred between the oxides although at 800° C. some reaction was observed. The results suggest that the reaction may be partly or wholly hydrothermal and probably depends for its success on the small amount of water retained by the arsenic pentoxide when precautions to exclude it are omitted.

The complex oxides resulting from these reactions were pyrolyzed by heating in porcelain boats in quartz tube furnaces capable of being evacuated or flushed with an air stream. The progress of the thermal decomposition and loss of arsenic was followed by observing the weight loss on the sample and removing portions from time to time for X-ray analysis. Chemical analyses were also performed on some of the products.

The powder diagrams were taken in 11.46 cm. Norelco cameras with CuK_α and CoK_α radiation for the nickel and cobalt complexes respectively.

RESULTS AND DISCUSSION

$M^{II}O.As_2O_5$ *Compounds*

These were well-defined compounds formed by high-temperature oxide reactions. The cobalt compound was obtained by heating a 1 : 1 cobalt monoxide – arsenic pentoxide mixture in a quartz tube at 500° C. for 3 days and was a bright purple color. The powder diffraction pattern agrees with that obtained by Magnéli (6) and could be indexed as hexagonal with unit-cell dimensions of $a = 4.773$ Å, $c = 4.494$ Å (Table I).

Powder diagrams of the $NiO.As_2O_5$ prepared by direct reaction of the oxides at 500° C. for 10 days showed several lines which did not appear in the $CoO.As_2O_5$ pattern. However, these lines decreased gradually in intensity on heating so that after 6 hours at 700° C. under vacuum they were completely absent. It was possible to index the pattern as hexagonal with unit-cell dimensions of $a = 4.759$ Å, $c = 4.431$ Å. The diffraction patterns and density data are recorded in Table II.

The two compounds are clearly isostructural and have the $PbO.Sb_2O_5$ structure (9) previously assigned to $CoO.As_2O_5$ by Magnéli.

$2M^{II}O.As_2O_5$ *Compounds*

Reactions between cobalt or nickel oxide and arsenic pentoxide in 2 : 1 and 3 : 1 ratios at 800° C. produced mainly $M^{II}O.As_2O_5$ but the diffraction patterns showed some lines which were later attributed to the $2M^{II}O.As_2O_5$ compounds. The amount of information obtainable from these patterns was limited by contamination of the sample resulting mainly from the severe attack of the quartz by the arsenic pentoxide at the high temperature.

Vacuum pyrolysis experiments on $NiO.As_2O_5$ produced no new phase after 12 hours at 710° C. with removal, grinding, and sampling at intervals of 2 hours. A further heating

TABLE I

POWDER DIFFRACTION PATTERN OF $CoO.As_2O_5$

(Hexagonal; $a = 4.773 \pm 0.002$ Å, $c = 4.494 \pm 0.002$ Å (cf. $a = 4.766$ Å, $c = 4.493$ Å obtained by Magnéli (6)); Fe-filtered Co radiation, $\lambda_{\alpha_1} = 1.78890$ Å; camera diameter, 11.46 cm.; cutoff 20 Å; temp. 24° C.; $\rho_{calc} = 5.71$ g./cc.; $z = 1$.)

I/I_1	$hk.l$	d_{obs} (Å)	d_{calc} (Å)
20	00.1	4.46	4.49
3	10.0	4.12	4.13
100	10.1	3.06	3.04
55	11.0	2.61	2.61
5	00.2	2.24	2.25
50	11.1	2.11	2.11
40	20.1	1.88	1.88
90	11.2	1.63	1.64
60	21.1	1.470	1.475
20	10.3	1.406	1.408
65	30.0	1.375	1.378
15	30.1	1.315	1.317
25	11.3	1.268	1.269
20	20.3	1.211	1.213
20	22.0	1.191	1.193
35	30.2	1.172	1.175
20	22.1	1.152	1.153
10	00.4	1.123	1.122
50	31.1	1.111	1.111
45	21.3	1.081	1.081
70	22.2	1.053	1.054
40	11.4	1.016	1.016
25	40.1	1.007	1.007
30	22.3	0.9333	0.9332
60	32.1	0.9278	0.9279
70	31.3	0.9103	0.9104
85	41.0	0.9020	0.9020

for 5 hours at 760° C. gave a material which on X-ray powder analysis showed a series of new lines together with some NiO and $NiO.As_2O_5$. A plot of per cent loss of weight against time of pyrolysis showed no inflection at the 2 : 1 composition under these conditions. By repeating the pyrolysis at a temperature of 720° C. the necessary weight loss was achieved in 230 hours but again it was impossible to reach equilibrium conditions. Powder photographs in this composition range were ill-defined at best. Pyrolysis in air gave the same decomposition products at about 920° C. but no better diffraction patterns were obtained. The material approximating in composition to $2NiO.As_2O_5$ had an ocher-yellow color as compared with the yellow-green of the 1 : 1 compound.

Similar experiments on the pyrolysis of $CoO.As_2O_5$ gave comparable results with a rather poorly defined dark purple 2 : 1 compound after 40 hours' heating at 736° C. under vacuum.

By careful selection of lines in the powder diagrams and elimination of lines from other phases identified in the system it is possible to suggest an orthorhombic symmetry for $2CoO.As_2O_5$ and $2NiO.As_2O_5$ having unit-cell dimensions of $a = 8.16$ Å, $b = 8.56$ Å, $c = 9.16$ Å for the cobalt compound, and $a = 8.12$ Å, $b = 8.52$ Å, $c = 9.29$ Å for the nickel compound. Interplanar spacings, indices, and observed intensities of the powder diagrams are recorded in Table III.

The 2 : 1 compounds are not isostructural with $2PbO.Sb_2O_5$, which has the cubic pyrochlore form $a = 10.3$ Å (11), or with $2CaO.Sb_2O_5$, which has an orthorhombic weberite structure, $a = 7.28$ Å, $b = 7.44$ Å, $c = 10.18$ Å.

The results of these experiments do not entirely agree with those of Guérin and Masson

(5), who claimed that $NiO.As_2O_5$ decomposes *in vacuo* at 650° C. to give $2NiO.As_2O_5$ as a single phase. However, no attempt was made to substantiate their claim by published X-ray data and it may be that they also had a mixture in the 2 : 1 composition range.

TABLE II

POWDER DIFFRACTION PATTERN OF $NiO.As_2O_5$

(Hexagonal; $a = 4.759 \pm 0.002$ Å, $c = 4.431 \pm 0.002$ Å; Ni-filtered Cu radiation, $\lambda_{\alpha_1} = 1.5405$ Å; camera diameter, 11.46 cm.; cutoff 20 Å; temp. 24° C.; $\rho_{calc} = 5.82$ g./cc.; $\rho_{obs} = 5.82$ g./cc.; $z = 1$. Lines observed with I/I_1 of 15 and below are not included in the table.)

I/I_1	$hk.l$	d_{obs} (Å)	d_{calc} (Å)
60	00.1	4.41	4.42
20	10.0	4.08	4.12
100	10.1	3.00	3.02
80	11.0	2.37	2.38
80	11.1	2.09	2.10
70	20.1	1.86	1.87
90	11.2	1.62	1.62
70	21.1	1.467	1.470
25	10.3	1.388	1.390
70	30.0	1.369	1.374
20	30.1	1.310	1.312
25	11.3	1.253	1.255
20	20.3	1.200	1.200
20	22.0	1.188	1.190
25	30.2	1.166	1.168
50	31.1	1.106	1.107
40	21.3	1.072	1.072
55	22.2	1.048	1.048
55	40.1, 11.4	1.003	1.004, 1.004
25	32.1	0.9242	0.9242
20	41.0	0.8990	0.8994
20	41.1	0.8814	0.8814
30	30.4	0.8625	0.8623
70	41.2	0.8335	0.8333
40	22.4	0.8108	0.8107
40	32.3	0.7964	0.7963
40	33.0	0.7930	0.7931
35	33.1	0.7807	0.7807

TABLE III

POWDER DIFFRACTION PATTERNS OF $2CoO.As_2O_5$ AND $2NiO.As_2O_5$

($2CoO.As_2O_5$—orthorhombic; $a = 8.16 \pm 0.01$ Å, $b = 8.56 \pm 0.01$ Å, $c = 9.16 \pm 0.01$ Å; Fe-filtered Co radiation, $\lambda_{\alpha_1} = 1.7889$ Å; $2NiO.As_2O_5$—orthorhombic; $a = 8.12 \pm 0.01$ Å, $b = 8.52 \pm 0.01$ Å, $c = 9.29 \pm 0.02$ Å; Ni-filtered Cu radiation, $\lambda_{\alpha_1} = 1.5405$ Å; camera diameter, 11.46 cm.; cutoff 20 Å; temp. 24° C.)

$2CoO.As_2O_5$				$2NiO.As_2O_5$		
I/I_1	d_{obs} (Å)	d_{calc} (Å)	hkl	I/I_1	d_{obs} (Å)	d_{calc} (Å)
50	4.22	4.27	020	40	4.22	4.26
20	4.03	4.08	200	10	4.04	4.01
20	3.74	3.78	120	10	3.76	3.77
50	3.47	3.50	121	35	3.48	3.50
100	3.16	3.13	022	100	3.14	3.14
90	3.06	3.05	202	90	3.06	3.06
90	2.96	2.95	220	90	2.94	2.94
20	2.51	2.49	023	30	2.51	2.50
40	2.26	2.26	231	30	2.27	2.26
40	2.08	2.08	033	30	2.09	2.09
20	2.02	2.03	024	45	2.04	2.04
60	1.90	1.89	142	45	1.88	1.88
50	1.67	1.65	341	50	1.65	1.65

$3M^{II}O.As_2O_5$ *Compounds*

Continuing the pyrolysis by increasing the temperature, compounds appeared in both systems corresponding to a metal oxide to arsenic pentoxide ratio of 3 : 1. At 750° C. this phase is perfectly stable in contrast to the behavior of the 2 : 1 compounds.

As an alternative approach to the preparation of these compounds the hydrates $3CoO.As_2O_5.8H_2O$ (erythrite) and $3NiO.As_2O_5.8H_2O$ (annabergite) were prepared and dehydrated. These minerals were synthesized by addition of $Na_2H.AsO_4.7H_2O$ solution to hot nickel nitrate or cobalt chloride solution using 0.1 weight per cent solutions in the preparation of the cobalt compound and 5% solutions for the nickel compound.[3] Powder photographs of the synthetic minerals were in excellent agreement with those of erythrite and annabergite.

On dehydration in an open crucible at 800° C. these hydrates yielded compounds having the same powder diagrams as those obtained from pyrolysis of the 1 : 1 compounds. The diffraction patterns could be indexed as orthorhombic with $a = 5.775$ Å, $b = 8.498$ Å,

TABLE IV

POWDER DIFFRACTION PATTERN OF $3CoO.As_2O_5$

(Orthorhombic; $a = 5.775 \pm 0.005$ Å, $b = 8.498 \pm 0.008$ Å, $c = 10.85 \pm 0.01$ Å; Fe-filtered Co radiation, $\lambda_{\alpha_1} = 1.7889$ Å; camera diameter, 11.46 cm.; cutoff 20 Å; temp. 24° C. All lines up to $\theta = 17°$, then $I/I_1 > 20$ up to $\theta = 55°$ included.)

I/I_1	hkl	d_{obs} (Å)	d_{calc} (Å)
25	100	5.81	5.77
13	101	5.11	5.10
10	110	4.80	4.77
18	012	4.53	4.57
40	020, 111	4.35	4.25, 4.37
30	021	3.96	3.96
40	003	3.69	3.62
65	112	3.49	3.58
30	121	3.24	3.26
40	103	3.06	3.06
85	031, 023	2.77	2.74, 2.75
75	210	2.72	2.73
75	004	2.69	2.71
30	211	2.64	2.65
100	202	2.57	2.52
25	033	2.24	2.23
30	040	2.15	2.18, 2.12
25	230	2.01	2.02
25	142, 134 310	1.87	1.87, 1.86 1.88
40	007, 314	1.553	1.551, 1.544
50	332, 206	1.521	1.528, 1.533
30	027, 251	1.454	1.456, 1.452
25	305	1.440	1.440
25	137, 422	1.327	1.324, 1.325
25	246	1.243	1.243
25	444	1.093	1.093

[3]*The very small crystallites obtained from the more concentrated nickel solution were developed by digestion in water at 100° C. for 1 week. It may be remarked that regardless of the relative concentrations of nickel and arsenate ion in solution only annabergite was precipitated. Similarly the residue obtained by digestion of varying quantities of basic nickel carbonate with arsenic acid exhibited only the diffraction pattern of annabergite although analyses indicated nickel to arsenic ratios of from 3:2 to 6:2. The amorphous nickel compound (probably the hydroxide) retained in these residues could not be removed by chemical means. On pyrolysis at 500° C., however, a face-centered cubic pattern appeared on the Debye–Sherrer diagrams. The unit-cell dimension of this compound (approximately 4.13 Å) was less than that of* NiO *(4.177 Å). That this pattern was directly associated with the amorphous nickel compound admixed with the annabergite was shown by the increase in intensity with increasing excess nickel content. This cubic compound was converted to* NiO *on pyrolysis at 800° C., when* $3NiO.As_2O_5$ *lines also appeared resulting from the decomposition of the annabergite. We were unable to obtain this cubic pattern by any other means.*

TABLE V

POWDER DIFFRACTION PATTERN OF $3NiO.As_2O_5$

(Orthorhombic; $a = 5.693 \pm 0.005$ Å, $b = 8.30 \pm 0.01$ Å, $c = 11.04 \pm 0.02$ Å; Ni-filtered Cu radiation, $\lambda_{\alpha 1} = 1.5405$ Å; camera diameter, 11.46 cm.; cutoff 20 Å; temp. 24° C.; $\rho_{calc} = 5.76$ g./cc.; $\rho_{obs} = 5.66$ g./cc.; $z = 4$. All lines up to $\theta = 17°$, then $I/I_1 > 20$ only up to $\theta = 33°$ included.)

I/I_1	hkl	d_{obs} (Å)	d_{calc} (Å)
20	100	5.70	5.70
7	101	5.04	5.11
5	110	4.71	4.69
7	012	4.46	4.60
60	111	4.31	4.32
7	020	4.07	4.16
30	021	3.91	3.89
40	003	3.67	3.69
75	112	3.48	3.57
35	121	3.19	3.20
30	103	3.03	3.09
30	113	2.94	2.90
5	122	2.80	2.86
80	004	2.75	2.75
80	210	2.68	2.69
25	211	2.62	2.62
100	202	2.54	2.53
30	033	2.21	2.21
50	015, 124	2.13	2.13, 2.13
45	230	1.99	1.98
25	042	1.94	1.94
25	310	1.85	1.85
30	026, 240	1.676	1.675
25	126	1.623	1.615
50	206	1.545	1.545
50	314	1.525	1.537
50	117	1.493	1.492
55	305	1.440	1.439
25	127	1.430	1.427

$c = 10.85$ Å for $3CoO.As_2O_5$, and $a = 5.693$ Å, $b = 8.30$ Å, $c = 11.04$ Å for $3NiO.As_2O_5$.

Powder diffraction data and results of density measurements are given in Tables IV and V.

In agreement with Guérin and Masson we found that $3NiO.As_2O_5$ cannot be hydrated to give annabergite even under 10 atm. pressure of water vapor.

$6M^{II}O.As_2O_5$ *Compounds*

The 3 : 1 compounds decompose under vacuum at about 850° C. to give the metal oxides but it was observed that an intermediate phase appeared in both the cobalt and nickel systems. The intermediate compounds were best prepared by pyrolysis in an air stream at 1000° C. The nickel compound was a bright green as compared with the dull green of $3NiO.As_2O_5$, and the cobalt compound a dark gray color in contrast to the dark powder blue of the $3CoO.As_2O_5$. Both gave good powder diffraction patterns. As a result of observations on weight losses during their formation and determinations of nickel and arsenic percentages it was concluded that these materials had a composition corresponding to $6M^{II}O.As_2O_5$. Results of analyses on two independently prepared samples of $6NiO.As_2O_5$ are given in Table VI. Although the figures do not appear to be very accurate allowance must be made for contamination by other compounds, which were just visible on the diffraction patterns.

It was at first considered possible to index the powder diagrams on the basis of hexagonal symmetry, the nickel compound having unit-cell dimensions of $a = 10.48$ Å, $c =$

TABLE VI

ANALYSIS OF $6NiO.As_2O_5$

	Calculated	Observed	
		(*a*)	(*b*)
% Ni	50.19	48.20	50.71
% As	22.09	21.11	20.22
Ratio Ni/As	3 : 1	2.9 : 1	3.2 : 1

12.03 Å. However, the cobalt powder diagram contained a rather broad intense line that was resolved into a doublet by annealing the sample at 800° C. in an evacuated quartz tube for 5 days. These lines could not be indexed in the hexagonal system.

In view of the isostructural nature of the other nickel and cobalt arsenates in the series it seems reasonable to assume that the 6 : 1 complexes are also structurally similar, and on the basis of this assumption the hexagonal symmetry assigned to the nickel complex has been discarded. However, the diffraction patterns of both compounds can be indexed by assuming orthorhombic cells, for which it is found that the reflections giving rise to the strong doublet in the cobalt compound overlap in the nickel compound producing a rather broad line. Observed intensities, interplanar spacings, and indices for these two compounds are recorded in Tables VII and VIII.

TABLE VII

POWDER DIFFRACTION PATTERN OF $6CoO.As_2O_5$

(Orthorhombic; $a = 5.724 \pm 0.005$ Å, $b = 9.418 \pm 0.01$ Å, $c = 12.07 \pm 0.01$ Å; Fe-filtered Co radiation, $\lambda_{\alpha_1} = 1.7889$ Å; camera diameter, 11.46 cm.; cutoff 20 Å; temp. 24° C. $I/I_1 > 20$ up to 30°, and $I/I_1 > 25$ up to 48° included.)

I/I_1	*hkl*	d_{obs} (Å)	d_{calc} (Å)
20	010	9.38	9.42
25	012	5.10	5.09
50	112	3.78	3.80
25	121	3.50	3.48
40	023	3.08	3.06
50	014	2.89	2.87
60	200	2.86	2.86
40	202	2.59	2.59
60	132	2.52	2.51
40	220	2.45	2.45
100	005	2.42	2.41
40	040	2.35	2.35
100	204	2.08	2.08
40	006	2.01	2.01
40	321	1.751	1.749
40	152	1.715	1.716
40	206	1.646	1.646
30	117	1.627	1.626
40	304	1.608	1.613
75	226	1.552	1.554
85	008	1.507	1.509
60	245	1.448	1.452
80	325	1.425	1.426
30	164	1.354	1.353
25	263	1.303	1.302
40	228	1.284	1.284
30	057	1.272	1.272
25	345	1.263	1.263
40	405	1.232	1.231
30	440	1.223	1.223

TABLE VIII

POWDER DIFFRACTION PATTERN OF $6NiO.As_2O_5$

(Orthorhombic; $a = 5.594 \pm 0.005$ Å, $b = 9.27 \pm 0.01$ Å, $c = 12.04 \pm 0.01$ Å; Ni-filtered Cu radiation, $\lambda_{\alpha_1} = 1.5405$ Å; camera diameter, 11.46 cm.; cutoff 20 Å; temp. 24° C.; $\rho_{calc} = 5.41$ g./cc.; $\rho_{obs} = 5.54$ g./cc.; $z = 3$. $I/I_1 > 15$ up to 30°, and $I/I_1 > 25$ from 30° to 83° included.)

I/I_1	hkl	d_{obs} (Å)	d_{calc} (Å)
40	010	8.98	9.26
50	012	5.01	5.05
20	102	4.08	4.16
70	112	3.73	3.75
45	023	3.04	3.03
60	014	2.84	2.86
50	114	2.55	2.55
30	024, 202	2.53	2.52
60	132	2.49	2.46
75	220	2.40	2.40
75	015	2.33	2.33
15	133, 222	2.24	2.24
15	230	2.08	2.08
100	204, 223	2.05	2.05, 2.06
20	310	1.829	1.830
20	215	1.791	1.791
40	017, 152	1.690	1.690, 1.690
25	216	1.604	1.605
35	304	1.586	1.586
25	323	1.559	1.558
20	061	1.531	1.533
85	018	1.483	1.481
85	028	1.429	1.430
25	164	1.335	1.335
30	165	1.265	1.267
30	0, 0, 10	1.204	1.205
40	446	1.030	1.028
30	277	0.9827	0.9826
35	4, 2, 11	0.8477	0.8476

SUMMARY

This study of the complex oxides occurring in the CoO/As_2O_5 and NiO/As_2O_5 systems has established the compounds $M^{II}O.As_2O_5$, $2M^{II}O.As_2O_5$, $3M^{II}O.As_2O_5$, and $6M^{II}O.As_2O_5$ as the only ones existing in the composition range $M^{II}O.As_2O_5$ to $M^{II}O$.

The 1 : 1 compounds are hexagonal and the 2 : 1, 3 : 1, and 6 : 1 compounds have been tentatively assigned orthorhombic symmetry. It is interesting to note that the unit-cell volumes of the 1 : 1 and 2 : 1 complexes are just less than those calculated for a close-packed oxygen-ion system (assuming $z = 6$ for the 2 : 1 compounds). The observed unit-cell volumes for the 3 : 1 and 6 : 1 compounds are greater than those required by a close-packed oxygen-ion array.

Both cobalt and nickel compounds exhibit similar thermal stabilities in that corresponding compounds in each system were observed to be stable over the same temperature range. *In vacuo* the 1 : 1 compounds decompose at 720° C. to give 3 : 1 compounds but an intermediate structure occurs in the composition range about 2 : 1. The 3 : 1 compounds decompose to give the 6 : 1 structure at 850° C., and at 850° to 875° C. the metal oxides are formed. In air at atmospheric pressure these decompositions are observed about 150° C. higher and even at 1000° C. the 6 : 1 complexes are stable. From this it would appear that the primary process in the decomposition of the arsenates is ejection of oxygen from the lattice.

ACKNOWLEDGMENTS

We should like to thank Dr. L. D. Calvert of this Division for the great interest he has shown in this problem and the assistance he has given with the crystallographic work.

We are also indebted to Dr. S. C. Robinson of the Mineralogy Division of the Department of Mines and Technical Surveys for a powder diagram of annabergite.

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PHOTOCONDUCTIVITY OF SOME POLYNUCLEAR AROMATIC HYDROCARBONS[1]

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ABSTRACT

The spectral response, voltage dependence, and intensity dependence of the surface photocurrent in naphthalene, terphenyl, pyrene, stilbene, and azulene have been measured. Pyrene and naphthalene have a high sensitivity for photoconduction at the long-wavelength edge of the optical absorption spectrum. In the spectral response of pyrene three peaks appear at 4475 Å, 4275 Å, and 4100 Å. It is suggested that these peaks are due to weak optical absorptions to energy levels which are highly efficient in promoting conduction. It is possible that a similar effect occurs in naphthalene, where maximum photoconductivity coincides with a weak absorption reported by McClure and Schnepp. Azulene only shows photoconductivity at wavelengths corresponding to absorption to the second singlet state.

INTRODUCTION

Recently a substantial amount of work has been devoted to the photoconductive properties of anthracene and tetracene (1, 2, 3, 4). Intensity, voltage, and spectral dependence as well as rise time, decay time, and temperature dependence of the photocurrent have been investigated thoroughly. More recently Lyons and Morris (5) published a note on the spectral dependences of a number of other polycyclic hydrocarbons. As the photocurrents were extremely low, they had to restrict themselves to measurements at wavelengths where a mercury arc provided a high enough intensity, i.e. to the wavelengths of the major mercury lines. In our laboratory the temperature dependence of the photocurrent in a number of compounds has been studied (6). Recently Lyons and Morris (7) reported experiments in which they used the qualitative resemblance of the spectral response of the photocurrent to the absorption spectrum to draw conclusions about the polarization ratio and thus about the assignments of this spectrum. In our measurements of the temperature dependence of the photocurrent we observed that some compounds photoconduct at wavelengths considerably longer than those within the region of the absorption spectrum. This was the case particularly for thicker crystals. With the aid of a 1000 w. xenon lamp as a strong ultraviolet source, it was decided to try to obtain a continuous spectral response for some of the compounds studied by Lyons and Morris and for some other ones that appeared to be of interest. The results of these measurements, and particularly those for pyrene which has been studied more extensively, are given in the present paper.

EXPERIMENTAL

Naphthalene, stilbene, and terphenyl single crystals were obtained from the Harshaw Chemical Company. A number of crystals of naphthalene for comparison were kindly grown for us by Dr. F. R. Lipsett in a Bridgeman furnace (8). No dependence on the source of the crystals was found. Azulene and pyrene crystals were measured as sublimation flakes. Thicker pyrene crystals were grown from a solution of pyrene in petroleum ether.

[1]*Manuscript received November 21, 1957.*
Contribution from the Division of Pure Chemistry, National Research Council of Canada, Ottawa, Canada. Issued as N.R.C. No. 4630.
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The light of a 1000 w. XBO 1001 (Osram) xenon lamp was passed through a Farrand 300 U.V. monochromator. The image of the exit slit of this monochromator was focused onto the specimen by means of a quartz achromat. A plane-parallel quartz plate placed in the light beam between achromat and crystal reflected part of the light onto a G.E. 935 vacuum photocell. Thus the current through the photocell is proportional to the intensity of the light incident on the crystal at any specific wavelength. The crystals were mounted on a quartz or teflon disk. Aquadag or silver paste contacts were painted round the ends of the crystal. All of the crystal and at least part of the contacts were illuminated. The teflon or quartz disks were mounted in a cell essentially the same as the one described by Chynoweth and Schneider (10), in which all insulation had been replaced by scrupulously cleaned teflon so as to prevent any spurious dark currents. From the cell went an insulated straight, rigid, and shielded lead to the input terminal of a Keithley 200 B micromicroammeter. The whole assembly was mounted on a board which slid on an optical rail and could also be adjusted in the two remaining directions; the monochromator was held in a fixed position on the same rail. With this setup currents down to about 5×10^{-14} amp. could be measured reproducibly within 2–3%.

The wavelength knob of the monochromator could be driven by a motor with gear assembly while the output of the micromicroammeter was recorded by a Varian G-10 recorder. At the beginning of each series of experiments the photoconduction assembly was replaced by a Moll thermopile (Kipp, Holland). This allowed calibration of the photocell. During a run readings of the current were continuously taken so as to allow subsequent correction for equal intensity input.

Intensity dependences were determined by placing neutral density filters between the monochromator and the deflecting quartz plate. The actual transmitted intensities could thus be read on the galvanometer of the photocell. The linearity of the photocell was checked with the thermopile and found satisfactory.

Voltage dependences were obtained by means of a 300 v. battery with a decade shunt of selected 1 meg resistances. All points for voltage and intensity dependence were taken at random.

In some pyrene crystals it was of interest to determine the absorption edge and the photoconductivity response. For these experiments the crystals were mounted on a quartz disk. The response curve was determined first and then without disturbing the crystal on the quartz disk the absorption edge was measured. These measurements were carried out in a Carey recording spectrograph. As only very small crystals were available, a condenser system was used to focus the beam from the exit slit of the Carey onto the crystal specimen. An image of the pinhole behind the crystal was focused on the entrance window of the photomultiplier. The objective lens of the condenser system was made adjustable so as to allow proper focusing outside the spectrophotometer. Lenses and specimen holder were mounted on a base which was made to fit onto the cell holder plate of the spectrophotometer compartment. For each spectrum a blank was run by removing the crystal from over the pinhole. Accurate positioning of the crystal could be carried out by looking through the objective lens, thus using it as a magnifying glass. By adjusting the slitwidths of the apparatus care was taken to ensure that about the same beamwidth was obtained in measuring spectra and spectral response curves.

RESULTS

All voltage and intensity dependences were found to be linear within the experimental error. For very low photocurrents sometimes a slight departure from the linearity of

the intensity dependence could be observed. Allowing more time between the measurements usually made any deviations disappear. Such departures from linearity could be super- or sub-linear and could never be reproduced from crystal to crystal.

The spectral dependences are given in Fig. 1. They are all corrected to an incident light intensity of about 20 μw./cm.^{2} The average beamwidth with which these curves have been measured was about 30 Å. Intensity considerations did not allow us to use polarized light in these experiments.

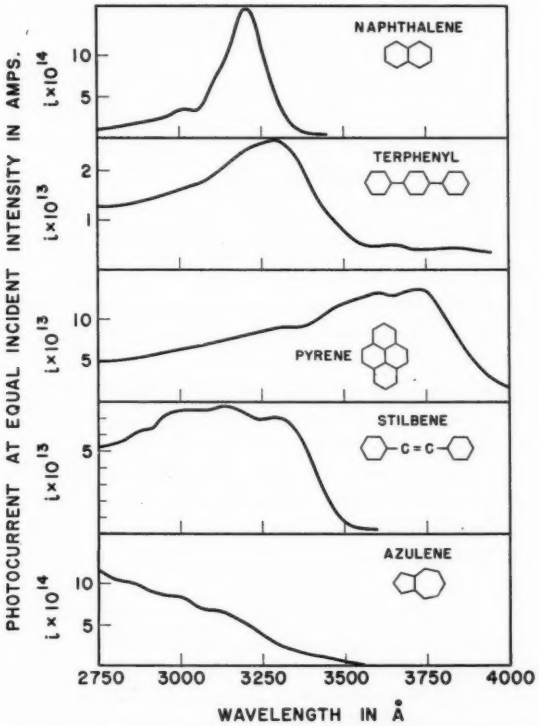

FIG. 1. Spectral response of the surface photocurrents in naphthalene, terphenyl, pyrene, stilbene, and azulene.

A feature of the spectral dependence of some of these compounds is their high sensitivity at the absorption edge. In this respect the present curves are in partial disagreement with those given by Lyons and Morris (5). However, light on the long-wavelength side of the absorption spectrum will be more strongly absorbed in the thicker crystals used in this work, and therefore lead to a higher photocurrent at these wavelengths.

The case of pyrene is most interesting, as even on the relatively thin sublimation flakes a structure in the spectral response could be observed beyond the region of the absorption spectrum of the crystal, which has its first peak at 3750 Å (11). It was therefore decided to investigate this material more closely, especially because the absorption edge lies in a spectral region where still an appreciable light intensity can be obtained without sacrificing too much resolution. It will be clear from Fig. 2 that the spectral response curves vary with the thickness of the crystals. At the long-wavelength edge of

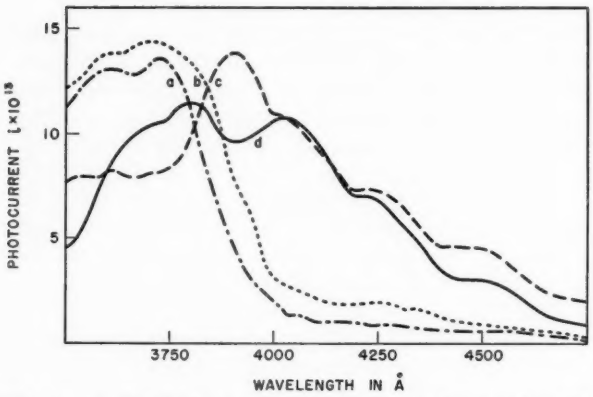

FIG. 2. Spectral response of the photocurrent of pyrene crystals of various thicknesses: (*a*) thickness 5 μ; (*b*) thickness 20 μ; (*c*) thickness 0.63 mm.; (*d*) sandwich-cell thickness 1.57 mm.

the absorption spectrum light will be absorbed throughout the crystal and contributions of deeper layers may be expected. Therefore the photocurrent at the absorption edge of the crystal will be favored with respect to the photocurrent at shorter wavelengths when the thickness of the crystals is increased. Curves *a* and *b* of Fig. 2 are for a thin (about 5 μ) and a thicker (20 μ) sublimation flake respectively. It is seen that the currents at wavelengths outside the absorption region are very low. Curve *c* applies to a crystal 0.63 mm. thick. The long-wavelength side of the curve is now very appreciable. Curve *d* is for a sandwich cell (4) of thickness 1.57 mm. with silvered contacts. Here also the long wavelengths make a greater contribution to the photocurrent. Contrary to anthracene, the bulk current in pyrene is of about the same magnitude as the surface current. A number of peaks appear at the long-wavelength side of the spectral response curves. One of these peaks is apparent. Although the curves have been calculated for an equal incident energy of 20 μw./cm.^{2} at all wavelengths, all this energy is not absorbed by the crystal. At longer wavelengths the major part is transmitted and absorbed by the black background. For this reason the absorption edges of the crystals were directly measured. Because the intensity dependence is linear the photocurrent is directly proportional to the amount of light absorbed:

$$i = \phi(I_e - I) = \phi I_0(1 - 10^{-D})$$

where i is the photocurrent, I_0 the incident intensity, I the transmitted intensity, D the optical density, and ϕ a proportionality factor we can call the "efficiency". Then:

$$\phi = (1/I_0)[i/(1 - 10^{-D})].$$

A plot of $i/(1-10^{-D})$ at constant incident intensity versus the wavelength will give a measure of the relative efficiency of the absorbed light in producing the photocurrent.

At wavelengths longer than 4100 Å no change in the absorption of a crystal could be detected. Owing to the large amount of scattered and reflected light in these thick crystals it is impossible to obtain an actual optical density at these wavelengths. As it would seem impossible for the crystal to photoconduct without the absorption of light it must be supposed that the crystals have a small but finite optical density as far out of the absorption region as 4750 Å. Fig. 3 gives a plot of $i/(1-10^{-D})$ at constant intensity

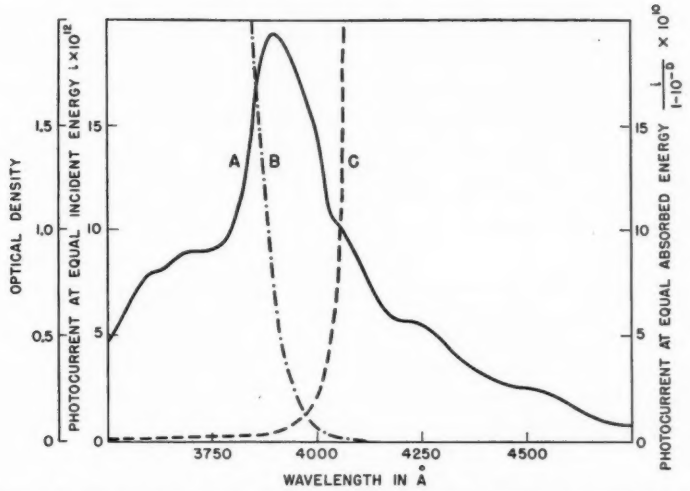

FIG. 3. Curve A shows the photocurrent as corrected for equal absorbed energy (scale at left). Curve B is the optical absorption edge (scale at left). Curve C gives the efficiency of the light in promoting photoconduction, i.e. the photocurrent corrected for equal absorbed energy (scale at right).

for a crystal with a very high apparent peak at 3900 Å. It will be seen that this peak is lost when the correction is applied. It will also be noted that light on the long-wavelength side of the absorption spectrum is very efficient in producing photoconduction. At the long-wavelength side of the response curve three peaks are observed: at 4475 Å, 4725 Å, and 4100 Å. Similar curves were obtained for a number of other crystals and within 25 Å the peak values all agree.

The fact that the 3900 Å peak is apparent could also be shown in another way. Comparison of Fig. 2 and Fig. 3 will show that its position and its magnitude changes with the thickness of the crystal. To rule out any peculiarities of the crystal, the following experiment was carried out. A crystal was mounted on a quartz disk and the spectral response curve determined with the quartz disk mounted against a black background. Then a layer of silver was evaporated on the back of the quartz plate without taking the crystal off, so as to create a mirror reflecting transmitted light and the spectral response curve was again determined. As is clear from Fig. 4 the apparent peak shifted from 3900 Å to 3950 Å.

A similar effect is observed with a background of white teflon. As the spectral response curves for the other compounds are all given for crystals on a white background it should be borne in mind that the long-wavelength side of the spectral dependence may be somewhat exaggerated.

It is of interest to note that in all materials except azulene photoconduction was detected at wavelengths where the optical absorption is negligible compared to its peak value. Stray light being ruled out by the use of suitable filters in the light beam, photoconduction was shown to take place in these materials as far out as 8000 Å, the limit of our instrument. No structure, except as mentioned for pyrene, could be observed, only a steady fall in sensitivity.

At the short-wavelength side of the spectral response curve some structure was always found. Although the accuracy at these wavelengths is rather poor owing to the low

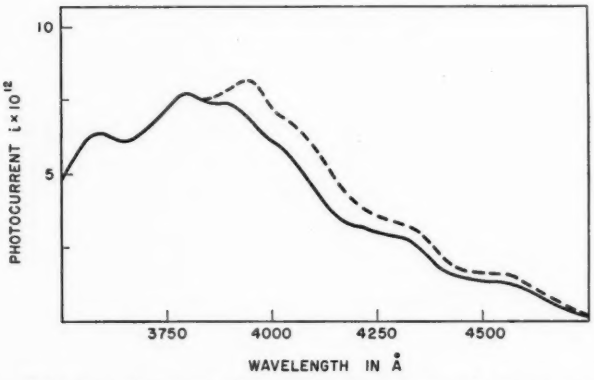

FIG. 4. Change of the spectral response of the surface photocurrent of a pyrene crystal with the reflective properties of the background. Solid curve: spectral response with a non-reflective background. Dotted curve: with a highly reflective background.

intensity of the incident light, peaks were usually observed at about 3600 Å and 3700 Å in pyrene.

In the course of obtaining absorption spectra for the pyrene crystals used in this work, it was observed that a weak absorption was present at the long-wavelength side of the absorption spectrum as given by Ferguson and Schneider (11). They observed the first main absorption band at 3750 Å. On crystals about 0.1 mm. thick, a shoulder on the main absorption was present with its center at 3832 Å.

DISCUSSION

From our results it appears that in pyrene and naphthalene light at the long-wavelength edge of the crystal absorption spectrum is very efficient in producing photoconduction. In naphthalene the peak of photoconduction appears at 3220 Å, where McClure and Schnepp (12) report a relatively weak absorption. However, in pyrene our measurements show peaks in photoconduction where there is no detectable absorption at all, even in crystals about 2 mm. thick.

There seem to be two possible explanations for this phenomenon. The first that comes to mind is the presence of an impurity. It is well known that commercial pyrene has a yellow color, and that this color persists after chromatographic purification through alumina (9). Chromatography through silica gel, however, yields completely colorless pyrene. After the first observations of the long-wavelength photoconduction, the chromatography through silica gel was repeated, but this did not change the appearance of the spectral response curve. Assuming an extinction coefficient of 10^4 for the impurity, to escape optical detection in a 1 mm. thick crystal, the concentration would have to be lower than 10^{-5} molar. If that impurity is then responsible for the photoconduction it must have a very high quantum yield. No organic photoconductors have been reported so far to possess this property. Moreover Carswell and Lyons (13) studied the influence of the addition of tetracene to anthracene on the photoconduction of anthracene. At the concentrations used (10^{-4} molar) no photoconduction by direct excitation of the tetracene could be observed. These considerations make it rather unlikely that an impurity can be held responsible for the observed effect.

We will therefore examine the other possibility, i.e. the photoconduction observed at the long-wavelength edge of the absorption spectrum is intrinsic and takes place by

direct excitation of the pyrene. Northrop and Simpson (14) have proposed levels of partly ionic character lying between the triplet and the singlet state. Terenin (15) introduced the concept of shared triplet levels, which would lie at the same energies. Lyons (16) considered the levels arising from the fact that an electron would be bound to a neutral molecule with the resulting hole on its neighbors. He thus concludes that there are a series of "ionized levels with bound electrons". For anthracene he calculated these levels to lie at energies lower and higher than the energy of the first singlet state. Murrell (17) pointed out that charge-transfer states too might be considered in this respect. All these levels have been suggested to be responsible for the electrical conduction in organic materials.

Ferguson and Schneider (11) report that the fluorescence of crystalline pyrene has its origin far below the first singlet state and propose to explain this by a charge-transfer process which would be facilitated by the close proximity of the pyrene molecules in the crystal. Contrary to naphthalene and anthracene, the molecules in the pyrene crystal lattice occur in pairs. Lyons (16) suggests that the absorption at 3339 Å as found in naphthalene (12) might be a direct observation of a transition to an ionized state.

At present it is still rather difficult to choose between the various mechanisms of photoconduction proposed by the different authors. Much more experimental work is needed to elucidate the exact nature of the transitions that can apparently take place between the ground state and some excited species with an energy lower than the singlet state. From the present work, however, the following conclusions can be drawn for crystalline pyrene:

A finite absorption exists between 4750 Å and the optically measured long-wavelength limit of the ultraviolet absorption spectrum. In this absorption, peaks appear at 4475 Å, 4275 Å, and 4100 Å. The transitions that take place in this region lead to states that are highly active in producing conduction, as is clear from the efficiency plot in Fig. 3. The peaks are at wavelengths between the absorption limit and the wavelengths of the fluorescent light as found by Ferguson and Schneider (11).

Similar conclusions can probably be drawn for naphthalene, where McClure and Schnepp (12) and various other workers reported weak absorptions in the region of maximum photoconductivity, as reported in this work.

For stilbene and terphenyl the crystal spectra so far are not available. The case of azulene is interesting because in first approximation the photoconductive response appears to coincide with the absorption to the second singlet state as measured by Sidman and McClure (18) in a solid solution of naphthalene. No photoconduction was found in the region of the absorption to the first singlet state. It is of interest to note that Beer and Longuet-Higgins (19) as well as Viswanath and Kasha (20) found that azulene does not fluoresce when it is irradiated in its first absorption band, but that it does fluoresce when irradiated in the second absorption band. Apparently the same mechanism that inhibits fluorescence also inhibits photoconduction.

The observation of photoconduction at longer wavelengths than the absorption spectrum may be useful to solve the problem of the apparent discrepancy between the thermal and optical activation energy. Pick and Wissman (21) showed that the thermal activation energy for naphthalene semiconduction in a high vacuum is 3.7 ev. This agrees well with the optical threshold energy as found in this work for naphthalene: 3400 Å $\approx$ 3.65 ev. Inokuchi (2) found for pyrene bulk currents, where gas effects will be limited, 2.4 ev., while the optical threshold appears to be at 4750 Å $\approx$ 2.61 ev. The threshold has been taken as the wavelength where the photoconductive sensitivity is approximately one hundredth of its peak value in crystals of about 1 mm. thickness. In view of the extended

long-wavelength tail, however, the concept threshold becomes rather vague, and in this respect Northrop and Simpson's idea (14) of a large number of levels, of which the higher ones contribute more to the conduction than the lower ones, becomes attractive.

ACKNOWLEDGMENTS

The authors are indebted to Dr. L. E. Lyons for the opportunity of reading his manuscript before its publication. Thanks are due to Dr. J. N. Murrell with whom we had some interesting discussions.

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SOME NEW FLUORIDE COMPLEXES OF TRIVALENT TITANIUM[1]

NORMAN F. H. BRIGHT[2] AND JOSEPH G. WURM[3]

ABSTRACT

Three new complex fluorides of trivalent titanium have been isolated from the products of electrolysis, under an inert atmosphere, of molten baths of KCl, NaCl, or mixtures of KCl and NaCl, containing either K_2TiF_6 or Na_2TiF_6. Electrolytic baths containing a mixture of KCl and NaCl with either K_2TiF_6 or Na_2TiF_6 yielded a violet-colored, face-centered cubic compound identified as K_2NaTiF_6, which was virtually insoluble in water and amenable to electrostatic separation from the metallic titanium also produced in the electrolysis. Baths containing molten mixtures of K_2TiF_6 and KCl gave a pale violet compound K_3TiF_6, which was slightly soluble in water. Baths containing Na_2TiF_6 and NaCl gave a deep violet-colored compound Na_3TiF_6 which was almost insoluble in water. The compounds K_3TiF_6 and Na_3TiF_6 have structures which approximate to cubic. The compounds K_2NaTiF_6 and Na_3TiF_6 are more stable to atmospheric oxidation than is K_3TiF_6. X-Ray diffraction patterns have been recorded for these compounds and some of their physical and chemical properties determined.

1. INTRODUCTION

The mechanism of titanium production by the electrolysis of fused alkali halide baths containing complex titanium salts of the type Na_2TiF_6 or K_2TiF_6 has recently been discussed by Wurm, Gravel, and Potvin (1). In the course of their work, certain products were obtained which yielded X-ray diffraction patterns corresponding to no previously published data. A preliminary notice of the isolation of the compounds giving rise to these patterns appeared in the above-mentioned publication. The present paper represents an amplification of this information and gives details of the X-ray and other data obtained on three new complex titanium fluorides which were isolated from the electrolytic products.

2. EXPERIMENTAL PROCEDURES

The alkali titanofluorides, having the formula M_2TiF_6, based on tetravalent titanium, are readily soluble in molten alkali chlorides in the temperature range 650° C. to 850° C., depending upon the particular compounds involved.

The electrolytic baths contained, at the start of the electrolysis, 20 to 30% of either Na_2TiF_6 or K_2TiF_6 in solution in a molten mixture of NaCl and KCl, having approximately the eutectic composition of 55% KCl, by weight. In certain later electrolyses, solutions of Na_2TiF_6 in NaCl and of K_2TiF_6 in KCl were used to yield products in which only one type of alkali ion was present in each case.

When these molten baths were subjected to electrolysis under an argon atmosphere, using a water-cooled stainless-steel cathode and a graphite crucible containing the melt as anode, the products of the electrolysis, examined after they had cooled and solidified, showed the following phenomena:

(*a*) Surrounding the cathode was a spherical core or "nut", composed of dendritic metallic titanium crystals embedded in a salt of deep violet color.

(*b*) Around the outside of this "nut" was the solidified salt bath, having a pale violet color.

[1]*Manuscript received November 1, 1957.*
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The cathodic "nut" was crushed and separated into its constituents by electrostatic means, yielding the titanium metal and the violet salt substantially free from each other. The crystalline salts were examined by the standard procedures of X-ray diffraction analysis, using CoK_α radiation and 57.3 mm. diameter Debye–Scherrer powder cameras. Occasionally, for greater precision in measuring line spacings, a 114.6 mm. diameter camera was used.

The solidified melt surrounding the "nut" was examined similarly, both directly as obtained and also after it was leached with boiling distilled water in the proportion of 2 g. of crushed melt to 25 ml. of water to dissolve the alkali chlorides and concentrate the remaining materials which carry the violet color. Residues of deep violet color, almost insoluble in water, were obtained by this leaching. These residues were analyzed chemically for sodium, potassium, total and trivalent titanium, chloride, and fluoride. Certain reference materials, used for preparing X-ray patterns in attempts to identify the unknown substances, were also analyzed chemically; these included the pure starting titanofluorides, Na_2TiF_6 and K_2TiF_6, and sodium titanate. All the chemical analyses referred to in this paper were done in the Chemical Laboratory of the Division of Mineral Dressing and Process Metallurgy, Mines Branch, Ottawa.

A résumé of the analytical procedures used is as follows:

Potassium and sodium.—Fluorine removed by evaporation of the sample with dilute sulphuric acid three times; titanium removed by hydrolysis of aqueous solution of product; potassium and sodium determined with a Perkin-Elmer flame photometer.

Fluorine.—HF steam-distilled off at 135°–140° C. from an aqueous perchloric acid solution of the sample. Fluorine determined amperometrically at pH = 7.0 using thorium nitrate solution previously standardized against NaF.

Chlorine.—Determined by potentiometric titration with 0.05 N $AgNO_3$ of a sulphuric/nitric acid solution of the sample. Less than one drop of reagent was required for a 0.2 g. sample, in those cases where chlorine was not expected to be present.

Titanium (total).—Residue from fluorine distillation reduced with zinc amalgam and titrated with ferric alum.

Titanium (trivalent).—Sample dissolved in aqueous sulphuric acid and titrated with ferric alum, all under an argon atmosphere. Alternatively, sample dissolved in ferric alum solution, and the reduced iron (equivalent to the trivalent titanium) titrated with standard potassium dichromate.

3. EXPERIMENTAL RESULTS

A comparison of the X-ray diffraction patterns of a considerable group of electrolytic products, using either Na_2TiF_6 or K_2TiF_6 as the starting material, in solution in mixed NaCl–KCl, showed that the principal products in all the solidified melt samples were sodium and potassium chlorides, each containing some of the other in solid solution. However, of greater interest was a group of weaker diffractions which was the same regardless of the initial material used. The violet materials, obtained as residues after the alkali chlorides were leached out, gave this same group of diffractions but in much greater strength. The same pattern was obtained from the violet material obtained from the cathodic "nut". In some of the leached products, no other pattern was detectable, and thus, presumably, the material giving rise to this set of diffractions was reasonably pure in these particular products.

The chemical analyses of the insoluble residues resulting from the water leaching of the electrolytic fusion products using K_2TiF_6 or Na_2TiF_6 with the mixed alkali chlorides are given in Table I. The two analyses obviously correspond to the same substance.

TABLE I

Element	Product using Na_2TiF_6 as starting material, % by weight	Product using K_2TiF_6 as starting material, % by weight	Theoretical for K_2NaTiF_6, % by weight
Na	9.5±0.1	9.5±0.1	8.74
K	27.5±0.1	27.4±0.1	29.72
Ti (total)	17.7±0.25	(i) 17.7±0.25 (ii) 17.6±0.25 Mean 17.7±0.25	18.21
Ti (trivalent)	17.7±0.5	17.6±0.5	18.21
F	40.2±0.25	43.1±0.25	43.33
Cl	None detectable	None detectable in 50 mg. sample	Nil

It can be seen from these analyses that the molecular formula for either material is very close to K_2NaTiF_6. The theoretical figures for this compound are also given in Table I.

From the chemical data alone, however, the material could equally well be a mixture of K_3TiF_6 and Na_3TiF_6 in the proportion of approximately 2 : 1. It therefore remained to determine whether this material (to which has been assigned the formula K_2NaTiF_6) is, in fact, a discrete compound in its own right, or merely one particular composition in a solid-solution series K_3TiF_6–Na_3TiF_6, should such a series exist. The fact that the same composition was obtained using either K_2TiF_6 or Na_2TiF_6 in molten NaCl–KCl as the starting material strongly supports the view that a single compound was present, rather than merely one particular composition in a solid-solution series. If it were a member of a solid-solution series, one might expect to obtain different compositions in the two cases. The matter was resolved with reasonable certainty by studying the products of electrolyses in which either K^+ or Na^+ ions were the sole alkali ions present.

The material obtained from the electrolysis of Na_2TiF_6 in NaCl was a deep violet in color, virtually insoluble in water, and gave the analysis given in Table II. This analysis corresponds very closely to Na_3TiF_6, and the titanium is all in the trivalent state, in accordance with the color of the material.

TABLE II

Element	% by weight	Theoretical for Na_3TiF_6
K	None detectable	Nil
Na	29.9±0.1	29.88
Ti (total)	20.2±0.25	20.74
Ti (trivalent)	20.2±0.5	20.74
F	49.7+0.25	49.38
Cl	0.034	Nil

The preparation of the corresponding potassium compound was more troublesome, since the material obtained by leaching out the KCl was readily oxidized in air. By evaporation of the water under an argon atmosphere, however, a product was obtained which contained either some unchanged or regenerated K_2TiF_6, a trace of residual KCl, and a compound of pale violet color, slightly soluble in water. In the analysis of this material, the chloride present was used as a measure of the KCl, the tetravalent titanium (i.e. total titanium minus trivalent titanium) used as a measure of the K_2TiF_6 present, and the remainder of the composition calculated accordingly. The results of this analysis are given in Table III.

The molecular formula of the compound calculated on this basis is $K_{2.997}TiF_{5.994}$,

TABLE III

Element	% by weight
Na	None detected
K	41.6±0.1
F	40.7±0.25
Cl	0.02
Ti (total)	17.1±0.25
Ti (trivalent)	15.4±0.5
Ti (tetravalent)	1.7 (by difference)

i.e. K_3TiF_6, and the composition of the product then works out at K_3TiF_6, 90.9%; K_2TiF_6, 8.4%; KCl, 0.34%.

When this product was examined by microscope, a very small amount of KCl was visible. Approximately 10% of colorless needle-shaped crystals were observed, having one refractive index $\omega = 1.475$ and the other (ϵ) slightly lower; this is in accord with the known optical properties of K_2TiF_6. The remaining material, about 90%, had a refractive index of approx. 1.406 and was slightly anisotropic. These proportions are in excellent accord with the above chemical analyses.

The material to which the formula K_2NaTiF_6 has been assigned was strictly isotropic optically and had a refractive index of 1.408. The compounds Na_3TiF_6 and K_3TiF_6 were both slightly birefringent, Na_3TiF_6 having refractive indices of $\omega = 1.387$ and $\epsilon = 1.382$, and K_3TiF_6 having refractive indices of $\omega = 1.406$ and $\epsilon =$ slightly lower than 1.406.

The mixed potassium–sodium material gave a face-centered cubic pattern based on a

TABLE IV

X-RAY POWDER DIFFRACTION PATTERN OF COMPOUND K_2NaTiF_6

(*hkl*)	Mean observed intensity*	Mean observed *d*-spacing, Å	Calculated† *d*-spacing, Å
111	35	4.8362	4.8306
002	15	4.1853	4.1835
022	100	2.9519	2.9581
113	7	2.5133	2.5227
222	50	2.4114	2.4153
004	90	2.0871	2.0917
133	3	1.9205	1.9195
024	8	1.8657	1.8709
224	50	1.7042	1.7079
115, 333	15	1.6064	1.6102
044	60	1.4766	1.4791
135	8	1.4088	1.4143
006, 244	5	1.3861	1.3945
026	25	1.3224	1.3229
335	3	1.2825 (?)	1.2759
226	10	1.2597	1.2614
444	25	1.2066	1.2077
117, 155	7	1.1704	1.1716
046	5	1.1571	1.1603
246	40	1.1167	1.1181
137, 355	5	1.0907	1.0893
008	15	1.0449	1.0459
228, 066	25	0.98562	0.98605
048	35	0.93561	0.93545
119, 357	5	0.91824	0.91839

**Strongest line assessed visually as 100.*

†Based on a cubic cell edge of 8.3669 Å.

TABLE V

X-RAY DIFFRACTION PATTERN OF THE COMPOUND Na_3TiF_6

Line No.	Observed intensity*	Observed *d*-spacing, Å	Line No.	Observed intensity*	Observed *d*-spacing, Å
1	50	4.646	26	5	1.438
2	20	4.525	27	12	1.415‡
3	60	3.976	28	10	1.391
4	8	3.566	29	20	1.357†
5	100	2.837†	30	5	1.313
6	20	2.765	31	5	1.281
7	40	2.496	32	20	1.265
8	40	2.427	33	10	1.249
9	60	2.393	34	10	1.234
10	5	2.330	35	10	1.216
11	30	2.216	36	10	1.193
12	30	2.155	37	5	1.169
13	90	1.999	38	5	1.154
14	10	1.947†	39	5	1.137
15	5	1.854	40	5	1.125
16	27	1.812	41	10	1.112
17	30	1.793	42	10	1.073
18	30	1.769	43	10	1.052
19	10	1.719	44	5	1.038
20	70	1.650	45	5	1.027
21	80	1.618	46	5	0.9906
22	40	1.608	47	5	0.9723
23	8	1.549	48	20	0.9473
24	5	1.500	49	10	0.9385
25	7	1.467	50	20	0.9322

**Strongest line assessed visually as 100.*
†Diffuse.
‡Doublet.

TABLE VI

X-RAY DIFFRACTION PATTERN OF THE COMPOUND K_3TiF_6

Line No.	Observed intensity*	Observed *d*-spacing, Å	Line No.	Observed intensity*	Observed *d*-spacing, Å
1	35	4.978	18	7	1.678
2	20	4.355	19	5	1.629
3	40	3.076	20	5	1.544
4	100	3.024	21	30	1.517
5	5	2.761	22	10	1.383
6	5	2.643	23	5	1.340
7	10	2.496	24	5	1.246
8	10	2.403	25	3	1.187
9	5	2.308	26	5	1.169
10	10	2.263	27	3	1.158
11	40	2.186	28	3	1.122
12	17	2.106	29	3	1.031
13	10	1.994	30	3	1.012
14	5	1.902	31	3	0.9982
15	5	1.845	32	3	0.9799
16	40	1.773	33	3	0.9610
17	17	1.741	34	3	0.9504

**Strongest line assessed visually as 100.*

cell edge of 8.3669 Å. The *d*-spacings observed, together with the indices of the various reflections and the calculated *d*-spacings using the above cell edge, are given in Table IV.

The X-ray spacings for the compound Na_3TiF_6 are given in Table V. It can be shown

that the main diffractions conform approximately to a cubic arrangement but that some distortion either of cell edge or of angle has occurred to cause a departure from the true cubic structure. The crystallography was not studied further because no single crystals of this compound of sufficient size were obtained.

Similarly, the compound K_3TiF_6 gave the X-ray diffraction data shown in Table VI. These data also indicate a slight distortion from a cubic structure, though probably not in the same way as for Na_3TiF_6. Again the crystallography has not been studied further.

4. DISCUSSION

The question to be decided is whether the material to which has been assigned the formula K_2NaTiF_6 should properly be regarded as a compound in its own right, or whether it is merely one particular member in a solid-solution series of which the end members are the compounds Na_3TiF_6 and K_3TiF_6, if such a solid-solution series in fact exists.

It has been shown that both end members are slightly anisotropic optically, whereas the material containing both potassium and sodium is strictly isotropic. This is strong, though not conclusive, evidence that K_2NaTiF_6 is a definite compound, since certain cases are known in which an optically isotropic member of a solid-solution series exists where neither end member is isotropic. A notable example of this exceptional optical behavior is in the melilite solid-solution series (2); here the end members, akermanite $2CaO.MgO.2SiO_2$ (3) and gehlenite $2CaO.Al_2O_3.SiO_2$ (4), are both anisotropic but an intermediate composition of approximately 65% akermanite: 35% gehlenite is isotropic.

If this behavior were applicable in the present instance, then the refractive index of the mixed sodium–potassium material would have to lie between the values given by the two end members, Na_3TiF_6 and K_3TiF_6. This is not the case, however, as the refractive index of K_2NaTiF_6 is 1.408 whereas the values for K_3TiF_6 are 1.406 and slightly below 1.406, and the values for Na_3TiF_6 are 1.387 and 1.382. In a solid-solution series, it is normal for the refractive index of an intermediate member to approximate to the value obtained by a linear interpolation between the values for the end members. In this case the intermediate material gives a value lying outside the range of values given by the end members; hence this is not analogous to the melilite behavior. This strongly suggests that the material K_2NaTiF_6 is to be considered as a compound and not as a member of a solid-solution series.

This optical evidence is further supported by the X-ray diffraction data, which show that the pattern given by K_2NaTiF_6 can be completely indexed according to a cubic unit cell; by contrast, neither K_3TiF_6 nor Na_3TiF_6 possesses a cubic structure, although both are close to it. Thus, the fact that neither the potassium nor the sodium compound is cubic, whereas the mixed potassium–sodium material is strictly so, is a cogent argument in favor of regarding K_2NaTiF_6 as a true compound. It may be mentioned by way of contrast that in the case of the melilites, referred to above, all members of the series, including the isotropic member, have a tetragonal structure with a c/a ratio in the range 0.6 to 0.7.

The above arguments support the validity of the contention that K_2NaTiF_6 is a definite compound in its own right. The strongest evidence, however, lies in the fact that the same composition is obtained regardless of whether K_2TiF_6 or Na_2TiF_6 is used as the starting material with the NaCl/KCl eutectic in the electrolytic preparation.

There are, thus, the following arguments in favor of the K_2NaTiF_6 being a definite compound:

(*a*) Its isotropic optical behavior, as contrasted with those of K_3TiF_6 and Na_3TiF_6.

(*b*) The value of its refractive index as compared with those of K_3TiF_6 and Na_3TiF_6.

(*c*) Its cubic X-ray pattern.

(*d*) The constancy of its chemical composition, irrespective of starting material.

Additional unequivocal evidence could have been provided by conducting liquidus determinations across the system K_3TiF_6–K_2NaTiF_6–Na_3TiF_6, when, if K_2NaTiF_6 were a true compound, a peak in the liquidus curve would have been obtained at that composition. It would also have been of interest to attempt to prepare the mixed potassium–sodium material from an appropriate mixture of the pure potassium and sodium compounds. However, the small quantities of material available precluded these two lines of investigation from being followed.

It is of interest to note that an exactly analogous series of compounds is known in the complex aluminofluorides, viz. K_3AlF_6, K_2NaAlF_6, and Na_3AlF_6; in this series, the mixed potassium–sodium compound is cubic and neither the sodium nor the potassium compound alone is cubic. Thus, K_3AlF_6 (potassium cryolite) is tetragonal with $c_0 = 8.468$ Å and $a_0 = 5.944$ Å (5); K_2NaAlF_6 (elpasolite) is cubic with $a_0 = 8.109$ Å (6); and Na_3AlF_6 (cryolite) is monoclinic (almost orthorhombic, and not far removed from tetragonal) with $a_0 = 7.80$ Å, $b_0 = 5.61$ Å, $c_0 = 5.46$ Å, and $\beta = 90°11'$ (7).

In addition, many other six-coordinated complexes of transitional elements containing two different alkali elements crystallize in the cubic system. The corresponding compounds containing one alkali element only in many cases either do not exist, or are not very stable, or do not crystallize in the cubic system. This behavior is due to the greater ease of packing three alkali ions of two different sizes (two larger, and one smaller) than of packing three ions of equal size.

The three compounds described in this paper are examples of new complexes in which the titanium is present in the trivalent state. Various compounds have been described in a more or less complete manner from a chemical viewpoint, in which the titanium in the trivalent condition was the starting material, and which were supposed still to contain the titanium in that state. In no case, however, was there any specific analysis for trivalent titanium in the product, but merely for total titanium content. Also, no crystallographic data (either optical or X-ray) have been provided for such compounds. These earlier publications included the following:

(*a*) Work by Piccini (8) in which compounds designated as $(NH_4)_3TiF_6$, K_2TiF_5, and $(NH_4)_2TiF_5$ were produced by the electrolytic reduction of fluotitanates in an aqueous solution of either NH_4F or KF. These compounds were in no case obtained in the pure state.

(*b*) Work by Petersen (9) in which $(NH_4)_3TiF_6$ was obtained by the cadmium reduction of aqueous K_2TiF_6 in warm hydrochloric acid solution with subsequent addition of NH_4F.

(*c*) Work by Stähler and his co-workers (10, 11) in which hydrated complexes of titanium trihalides were produced; these workers also prepared hydrated trivalent sulphates, oxalates, acetates, formates, and thiocyanates. In all cases the titanium was considered as forming part of a coordination complex.

(*d*) Work by Schumb and Sundström (12) in which ammine complexes of titanium di- and tri-chlorides were prepared.

In a recent patent (13), complexes containing divalent and trivalent titanium are claimed, but they were not isolated nor identified precisely.

Thus, in the present work, three new compounds have been described which are complexes containing trivalent titanium. They have been characterized by chemical analysis, optical data, and X-ray crystallographic study.

ACKNOWLEDGMENTS

The authors wish to express their thanks to members of the Mines Branch staff, especially to Miss E. M. Penner, Mr. L. G. Ripley, and Mr. R. C. McAdam for the difficult and painstaking chemical analyses done in connection with this work, and to Mr. Richard H. Lake for valuable assistance with the X-ray diffraction work.

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MOLECULAR REARRANGEMENTS IN THE REACTIONS OF OXYGEN ATOMS WITH OLEFINS[1]

R. J. CVETANOVIĆ

ABSTRACT

Reactions of oxygen atoms with propylene, butene-1, *iso*-butene, *cis*-butene-2, *trans*-butene-2, *cis*-pentene-2, and tetramethyl ethylene have been studied at room temperature and at pressures between 50 and 600 mm. The following generalizations can be made. The oxygen atom adds predominantly to the "less-substituted" carbon atom of the olefinic double bond to form a short-lived biradical which rapidly rearranges into isomeric epoxy and carbonyl compounds. Rearrangements involve migration of radicals (including H atoms) from the carbon atom to which oxygen is attached to the other carbon atom of the original double bond. Partly inhibited rotation around the original double bond also takes place. Migration of H atoms is exclusively internal. Migration of larger radicals, such as CH_3, is only partly internal: a large fraction of these radicals become completely detached from the rest of the molecule and the particular carbonyl compound is produced both by radical combination and by internal migration. The fragmentation resulting from the splitting off of a migrating radical is pressure independent. The final addition products formed are "hot" as a result of high heats of reaction and undergo decomposition if the excess energy is not removed by collisions. This second type of fragmentation is, therefore, pressure dependent. It is very extensive in the case of ethylene and appears to be completely suppressed in the investigated pressure range in the case of more complex olefins (possessing a greater number of degrees of freedom) such as butenes and higher homologues. Propylene exhibits an intermediate behavior. For orientation of addition of oxygen atoms a carbon atom of an olefinic double bond to which CH_3 is attached is "less substituted" than a corresponding carbon atom to which C_2H_5 is attached.

INTRODUCTION

In a previous publication (1) some preliminary results of a study of the reactions of oxygen atoms with a number of butenes have been briefly reported. This investigation has two distinct objectives: (1) to establish the general mechanism and the type of products formed, and (2) to obtain information on the rates of these reactions. In the present paper the first of the two aspects of the investigation is presented in detail and is extended to some further olefins studied in the meantime.

This work is a part of a more extensive study of the reactions of oxygen atoms with different organic compounds. The reactions with ethylene (2) and acetaldehyde (3) have already been described, while the results obtained with some other types of compounds will be published at a later date. Oxygen atoms are generated by mercury-photosensitized decomposition of nitrous oxide (4) and are probably in their ground, triplet $O(^3P)$, state. The amount of nitrogen formed gives a direct quantitative measure of the oxygen atoms generated and serves as an internal actinometer.

EXPERIMENTAL

A conventional-type high-vacuum apparatus was used. It incorporated a cylindrical silica reaction cell, 5 cm. in diameter and 10 cm. long, an all-glass circulating pump supported on teflon bearings, a LeRoy still (5), and a constant volume burette with a copper oxide tube and outlets for sampling tubes connected with it. Two low-pressure mercury lamps were placed one at each end of the reaction cell and were used singly or simultaneously as the source of mercury resonance radiation.

For the analysis of products use was made of the LeRoy still (for a preliminary separation into fractions), the copper oxide tube in conjunction with the constant-volume

[1]*Manuscript received November 27, 1957.*
Contribution from the Division of Applied Chemistry, National Research Council, Ottawa, Canada.
Issued as N.R.C. No. 4638.

burette (for the analysis of the non-condensables), gas–liquid chromatography (GLC), infrared and mass spectroscopy. An attempt was made, whenever possible, to verify the qualitative identification of the products by directly comparing the GLC relative elution times (6) and the infrared and mass spectra for the unknown product (after separation on GLC) and for a standard sample of the corresponding compound. In one or two cases a standard sample was not available and the identification was based on the comparison of the mass and infrared spectra with the existing literature data. In the early stages of the investigation, before the type of products formed was established, relative elution times were determined for a number of different C_4H_8O isomers and, thus, several possibilities were readily ruled out. A 10 ft. column of dinonyl phthalate on glass spheres (passing 270 mesh) was used, and the GLC apparatus differed from the one previously described (7) in that the low pressure (*ca.* 30 mm.) at the outlet of the column was maintained constant by inserting a suitable *internal* capillary in the lead to the high-vacuum pump and not by an external leak. A better stability was obtained in this manner and a gradual deterioration in the performance of the high-vacuum pump was prevented. The inlet pressure was maintained at 14 p.s.i. and the column temperature varied from 25° to 110° C. depending on the volatility of the products.

Best available grades of reactants were used after thorough degassing and bulb-to-bulb distillation *in vacuo*. N.B.S. samples of *cis*-pentene-2 and 3-methylheptane were kindly supplied by the Stanford Research Institute. *cis*-C_4D_8-2 was prepared by Dr. L. C. Leitch of these laboratories. Molecular oxygen was produced by heating reagent grade $KMnO_4$.

In the experiments carried out a large excess of nitrous oxide was used (100 to 600 mm. N_2O and usually only a few millimeters of the olefin). The ratio of the over-all quenching efficiency of an olefin and nitrous oxide is about 2 (8). The quantum yield of decomposition of nitrous oxide, however, is quite high (3) while that of olefins is as a rule very low, especially at the high total pressures used (9). Experimental conditions, therefore, could be readily adjusted so as to eliminate complications from direct quenching decompositions of olefins. By not extending the reactions to too high conversions, secondary reactions involving the products could also be avoided. Actually no trends in the rates of formation of the products per oxygen atom consumed were observed, except at very high conversions, after most of the olefin was consumed.

RESULTS

Experiments carried out with a number of hydrocarbons have shown that in general three types of reactions may be expected between the ground-state oxygen atoms and olefins: (1) addition of atoms to the olefin to form addition products, (2) fragmentation of the initially produced addition products, and (3) hydrogen abstraction.

Hydrogen Abstraction

At room temperature at least, and with the olefins studied so far, no evidence was found of any direct hydrogen abstraction by oxygen atoms. This finding is in agreement with the observed much higher rates of addition of oxygen atoms to the olefinic double bond relative to the hydrogen abstraction from paraffins. Thus, for example, the addition of oxygen atoms to *cis*-pentene-2 was found to be 43 times faster than the reaction of oxygen atoms with 3-methylheptane. It is conceivable, however, that with certain olefins a small amount of direct hydrogen abstraction takes place even at room temperature and that at elevated temperatures the abstraction reaction might become quite important.

Reaction of Oxygen Atoms with Propylene

In the reactions reported in the present communication the observed addition compounds, isomeric epoxides and carbonyl compounds, are the major reaction products, although a certain amount of fragmentation occurs as well. In this respect propylene exhibits a behavior intermediate between that of ethylene on one side and higher alkenes on the other. In the case of ethylene (2) extensive fragmentation takes place (CO yield ≈ 0.5). At best very little ethylene oxide is formed, and while the remainder of the oxygen is recovered mainly in the form of aldehydes at least a large fraction of these results from free-radical reactions. There is, however, an indication of a pressure effect, although this is quite small: there is a slight increase in the yields of aldehyde and ethylene oxide and a decrease in CO with increasing pressure. In contrast to this, in the case of higher olefins, taking as an example butene-1, large amounts of α-butene oxide and *n*-butyraldehyde are formed by direct addition of oxygen atoms and subsequent molecular rearrangement, their yields are pressure independent between 100 and 600 mm. within the experimental error, and there is relatively little fragmentation. The main trends observed in the case of propylene are shown in Fig. 1. At higher pressures

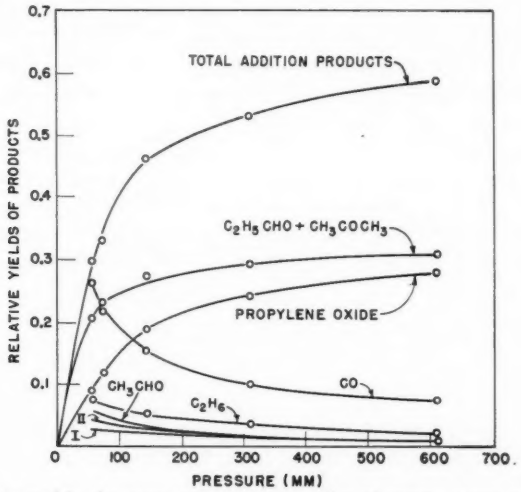


FIG. 1. Products observed in the room-temperature reaction of oxygen atoms with propylene at various total pressures. Curve I gives the yields of H_2 and also those of C_2H_4. Curve II gives the yields of CH_4. (For H_2, C_2H_4, CH_4, and CH_3CHO experimental points are not shown because of the mutual proximity and partial overlapping of the curves.)

increasing amounts of propylene oxide and propionaldehyde are formed and the character of the reaction approaches the one exhibited by butene-1, while at lower pressures fragmentation becomes more important and the reaction in many respects resembles that of ethylene. The pronounced pressure effect in the case of propylene is of particular interest and will be further discussed in the following section. With the chromatographic column used acetone could not be resolved from propionaldehyde, and total peak areas for the two compounds are plotted in Fig. 1. Infrared and mass spectra indicated large predominance and perhaps exclusive formation of the aldehyde. One separation was carried out on a 50 ft. tricresyl phosphate on firebrick column (120°) on which the two compounds completely resolved, and the ratio of the peak area of the aldehyde to that of acetone was about 9:1.

Formation of Addition Products

The addition products formed in the different reactions studied are summarized in Table I. The fractions of the addition products given in the table are based on GLC peak areas, taking the sum of the peak areas of all the addition products observed as unity. In some cases, as, for example, *cis*-β-butene oxide and *iso*-butanal as well as for *cis*-β-pentene oxide and 2-methylbutanal, the peaks partially overlapped and were approximately resolved graphically to obtain the individual peak areas. The last column in Table I gives the sum of the peak areas of all the fragmentation products observed by GLC analysis as a fraction of the total peak area of all the products (both addition and fragmentation). No attempt was made to identify the very small amounts of these fragmentation products in the cases where they were observed. In the case of butene-1 they seemed to consist largely of acetaldehyde and propionaldehyde.

TABLE I

PRODUCTS OBSERVED BY GLC ANALYSIS

(After removal of the unconsumed reactants and of any products of the same or greater volatility)

Reactant	Addition products[a]				Fragmentation products[b]
	Epoxides		Carbonyl compounds		
Propylene	Propylene oxide	0.50[c]	Propanal Acetone	0.50[c,d]	
Butene-1	α-Butene oxide	0.53	*n*-Butanal Methylethyl ketone	0.43 0.04	0.06
iso-Butene	*iso*-Butene oxide	0.54	*iso*-Butanal Methylethyl ketone	0.43 0.03	0.00
cis-Butene-2	*cis*-β-Butene oxide *trans*-β-Butene oxide	0.25 0.26	*iso*-Butanal Methylethyl ketone	0.23 0.26	0.02
trans-Butene-2	*cis*-β-Butene oxide *trans*-β-Butene oxide	0.15 0.33	*iso*-Butanal Methylethyl ketone	0.21 0.31	0.02
cis-Pentene-2	*cis*-β-Pentene oxide *trans*-β-Pentene oxide	0.23 0.31	2-Methylbutanal Methyl-*n*-propyl ketone Diethylketone	0.21 0.25[e]	0.06
Tetramethyl ethylene	Tetramethylethylene oxide	0.52	Pinacolone	0.48	0.08

[a] *The fractions are calculated from GLC peak areas taking the total area of all* addition *products as unity.*

[b] *The fractions are calculated from the total GLC peak area of the observed compounds other than the addition products taking the total peak area of* all *the products observed as unity.*

[c] *Extrapolated values for infinite pressure.*

[d] *Predominantly propanal (about 90%).*

[e] *Predominantly methyl-n-propyl ketone; some diethylketone is probably also formed (a small peak of the same elution time is observed; infrared and mass spectra, however, indicate a very low upper limit and perhaps absence of diethylketone).*

Formation of a restricted number of principal products in these reactions, mutually isomeric and of a molecular weight equal to that of the olefin used plus an oxygen atom, suggested strongly a direct addition of the atoms followed mainly by a molecular rearrangement rather than a free-radical process. This was substantiated by experiments in which two olefins were used simultaneously. In these experiments no new products were found but only those observed with the same two olefins when used singly, and their respective amounts were approximately proportional to the concentrations of the olefins used. Further information on the nature of these processes was obtained by studying the effect of additions of molecular oxygen.

Effect of Additions of Molecular Oxygen

Several experiments were carried out with *iso*-butene, butene-1, *cis*-butene-2, and tetramethyl ethylene in the presence of molecular oxygen. Initial pressures of 500 mm. N_2O, 7 to 15 mm. olefin, and 3 to 30 mm. O_2 were used.

In the case of *iso*-butene and butene-1 there was no or at best very little inhibition of the formation of the addition products even when the partial pressure of molecular oxygen was relatively quite high. The yields of aldehydes appeared to be slightly lowered and smaller amounts of some new products were also formed. In the case of *iso*-butene the latter amounted roughly to about 20% of the total product and probably were *tert*-butanol and acetone, although the identification was not certain. These two compounds were not found in the mercury-photosensitized reaction of *iso*-butene (60 mm.) in the presence of small amounts of O_2 but in the absence of N_2O. No attempt was made to study in detail these products or the mode of their formation.

In experiments with *cis*-butene-2 it was found that after a small amount of quenching by oxygen itself was taken into account approximately, the yields of *cis*- and *trans*-β-butene oxide and of methylethyl ketone were, within the analytical error, unaffected by the presence of molecular oxygen. On the other hand, the yield of ethane (produced normally in this reaction in small amounts, as discussed later) was rapidly suppressed and that of *iso*-butanal was reduced to about 20 to 25% of its value in the absence of oxygen and then remained independent of further oxygen additions. Simultaneously, appreciable amounts of methanol began to be formed. The effect of additions of O_2 on the composition of liquid products is shown in Table II. These results indicate that a large fraction of *iso*-butanal is formed by radical combination but that, nevertheless, a certain amount is produced by internal migration of CH_3 radicals. Similarly, one experiment with tetramethyl ethylene in the presence of about 40 mm. of O_2 showed a substantial reduction but not complete suppression of pinacolone while the yield of the epoxide appeared to be unaffected.

TABLE II

THE EFFECT OF MOLECULAR OXYGEN ON LIQUID PRODUCTS IN THE REACTION OF O ATOMS WITH *cis*-BUTENE-2 (500 mm. N_2O, 7 mm. *cis*-C_4H_8-2; irradiation time 30 min. Fractions of the sum of the observed GLC peak areas are given.)

Run	pO_2, mm.	*trans*-β-C_4H_8O	*cis*-β-C_4H_8O	$CH_3COC_2H_5$	*iso*-C_3H_7CHO	CH_3OH
264	–	0.26	0.23	0.26	0.25	–
266	3.2	0.27	0.24	0.25	0.095	0.15
265	14.6	0.27	0.22	0.24	0.052	0.21
267	41.7	0.26	0.23	0.27	0.052	0.19

Effects of Irradiation Time and of Pressure

Effects of time of irradiation and of the total pressure were checked with butene-1 and *cis*-butene-2 and, in a less systematic manner, with some of the other olefins used. Within the experimental error the rates of product formation were found to be independent of irradiation time up to relatively high conversions. The results of experiments with constant small amount of *cis*-butene-2 (about 5 mm.) and nitrous oxide varying from 80 to 600 mm. are given in Table III. There was at best only a very slight decline at low pressures in the yields per oxygen atom consumed of the addition products, and their ratios remained constant (in these experiments total peak areas of *iso*-butanal plus *cis*-β-butene oxide were measured). The yield of C_2H_6 showed a slight decline at first;

TABLE III

THE EFFECT OF PRESSURE ON THE YIELD OF PRODUCTS IN THE REACTION OF O ATOMS WITH *cis*-BUTENE-2

	Relative rates						
Pressure, mm.	CO[a]	CH_4[a]	C_2H_6[a]	C_2H_4[a]	*trans*-β-Butene oxide[b]	*iso*-C_3H_7CHO + *cis*-β-butene oxide[b]	$CH_3COC_2H_5$[b]
82	0.041	Trace	0.097	0.009	0.19	0.39	0.18
105	0.035	Trace	n.d.[c]	n.d.[c]	0.18	0.36	0.18
205	0.035	Trace	0.094	0.005	0.22	0.41	0.21
406	0.038	Trace	0.073	0.004	0.20	0.39	0.20
608	0.046	Trace	0.072	0.002	0.19	0.41	0.20

[a]*Based on manometric measurements and mass spectrometer analyses.*
[b]*Based on GLC peak areas.*
[c]*Not determined.*

there was, however, a tendency for leveling off rather than for complete suppression of this product at still higher pressures. The nitrous oxide technique is not suitable for the study of these processes at quite low pressures because of the increasing importance of secondary phenomena. In the pressure range 50 to 600 mm. the ratio of the two major products from butene-1, α-butene oxide and *n*-butanal, remained constant—their absolute yields per oxygen atom consumed appeared also to be constant although a very slight pressure dependence might have been masked by a small random run-to-run variation in GLC response. With the other olefins occasional experiments with variable pressures did not show any significant pressure effects. Of the minor products, carbon monoxide seemed to show generally a slight pressure dependence; thus, with butene-1 its yield per oxygen atom consumed decreased from about 0.06 at a total pressure of 50 mm. to 0.03 at 600 mm.

The Extent of Fragmentation

The very small amounts of fragmentation products detected by GLC analysis (Table I) were thought at first (1) to indicate that fragmentation occurred only to the extent of a few per cent. Actually, it proved difficult to establish accurately the extent of fragmentation. A number of GLC calibrations showed that the observed addition products accounted only for about 70 to 80% of the oxygen atoms consumed and in some cases even less. The quantitative aspect of this result, however, is not entirely satisfactory. Apart from the likelihood that some hydrogen abstraction may occur, there is no certainty that all the addition products formed are quantitatively recovered, in spite of all the precautions. Also, it is somewhat difficult to obtain accurate GLC calibrations with the very small amounts involved, especially so with some of the substances formed in these reactions. An attempt was, therefore, also made to estimate the extent of fragmentation from the amount of other fragmentation products detectable.

The fragmentation products more volatile than nitrous oxide were separated on the LeRoy still into the non-condensables and the "C_2" fraction and then further analyzed. The results are given in Table IV and refer to experiments in which 300 mm. N_2O and small amounts of the olefin were used. No systematic analysis could be made for products of similar volatility to that of N_2O, such as C_3H_8, C_3H_6, etc. In some cases, infrared spectra were taken of the N_2O fraction and no additional peaks were observed; minor amounts of any substances present need not have been detected in this manner. Similarly, in the GLC analysis, minor amounts of substances eluting with the original olefin or of those much less volatile than the major products observed could have escaped detection.

TABLE IV

PRODUCTS MORE VOLATILE THAN NITROUS OXIDE
(non-condensables and "C_2" hydrocarbons)

Reactant	Rates per oxygen atom consumed		
	CO	CH_4	C_2H_6[a]
Butene-1	0.04	Trace	0.00
iso-Butene	0.03	Trace	0.00
cis-Butene-2	0.04	Trace	0.08
trans-Butene-2	0.04	Trace	0.08
cis-Pentene-2	0.03	Trace	0.015
Tetramethyl ethylene	0.02	Trace	0.15

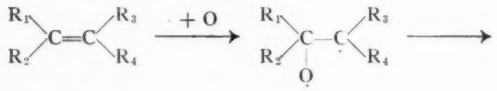
[a] *Mass spectrometer analyses of the* C_2H_6 *fraction indicated at best only trace amounts of* C_2H_4.

The appreciable amounts of ethane formed in some cases, as shown in Table IV, indicate that at least in some of the studied reactions the fragmentation is not negligible even when appreciable pressure effects are absent. With *cis*-butene-2, for example, an experiment in which a mixture of *cis*-C_4H_8-2 and a smaller amount of *cis*-C_4D_8-2 was used no C_2D_6 was formed but only CH_3CD_3 and C_2H_6. Ethane is, therefore, formed by combination of free methyl radicals. The results obtained in the presence of O_2 also showed that ethane and a large fraction of *iso*-butanal were formed by combination of free radicals, as already pointed out. On the basis of these results, the extent of fragmentation into free radicals at higher pressures can be estimated at about 30 to 35% (based on the consumption of oxygen atoms) for *cis*-butene-2 and in the case of tetramethyl ethylene probably as much as 60%. Such large fragmentation at higher pressures appears to take place when rearrangements which follow the addition of oxygen atoms involve migration of methyl radicals, but not (or at best only to a small extent) when H atoms migrate. It is significant that even when large fragmentation of this kind occurs the greater part of the free radicals recombine to form the same compound as produced by direct internal migration. Thus it would seem that the fragmentation involves entirely (or predominantly) only the splitting off of the migrating radicals.

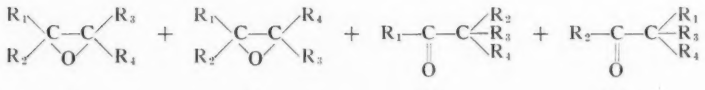
DISCUSSION

On the basis of the comparison of the addition products formed with butene-1, *cis*-butene-2, and *iso*-butene, the mechanism of addition of oxygen atoms to a CC double bond in alkenes was generalized in the preliminary communication (1) in the form of two rules. In view of the additional information available, these rules can now be amplified. The consistency of the results obtained in all the reactions of alkenes with oxygen atoms studied so far indicates that the addition products formed can in general be explained and predicted by assuming that: (1) an oxygen atom adds to one carbon atom of the double bond to form a biradical and this addition takes place in the case of unsymmetrical alkenes predominantly at the less-substituted carbon atom, and (2) the triplet thus formed degrades to the ground-state compounds in two ways: (*a*) by forming the corresponding epoxides without any internal rearrangement except a partially restricted rotation about the original double bond, and (*b*) by forming carbonyl compounds through migration of a particle (either a hydrogen atom or a radical) attached to the carbon atom carrying the oxygen atom to the other carbon atom of the original double bond. Migrating radicals may in the course of this process become to a smaller or greater extent detached from the molecule, as will be discussed later.

The following scheme for the reaction of oxygen atoms with a generalized olefin (A) illustrates the above rules. R_1, R_2, R_3, and R_4 are alkyl radicals or hydrogen atoms. The first C atom of the double bond is assumed to be "less substituted".

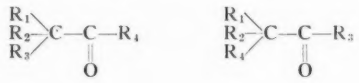


A B



I II III IV

Each of the compounds I to IV is produced in substantial quantities: these four compounds are the main and may be the exclusive addition products formed. (Compounds III and IV will be identical if $R_1 = R_2$, and similarly I and II if either $R_1 = R_2$ or $R_3 = R_4$.) It is possible also that some addition of oxygen atoms may take place at the "more-substituted" carbon atom, in which case minor quantities of carbonyl compounds V and VI will also be formed. In all the cases studied so far, addition to the "more-substituted" carbon atom has been of minor importance inasmuch as it occurred at all.



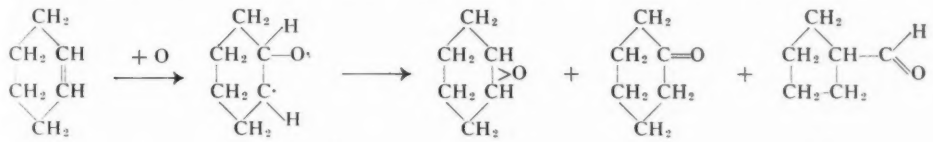
V VI

This reaction scheme has been illustrated in the preliminary communication (1) by the example of *cis*-butene-2, a symmetrical olefin. The predicted and observed addition products in this case are *cis*- and *trans*-2,3-epoxybutane, methylethyl ketone (formed through migration of an H atom) and *iso*-butanal (formed through migration of a CH_3 radical). The same products are to be expected and have been observed with *trans*-butene-2. In the case of *iso*-butene the main addition products are *iso*-butene oxide and *iso*-butanal and, therefore, oxygen atoms add predominantly to the "less-substituted" carbon atoms of the double bond. Addition to the "more-substituted" carbon atom of the double bond would require formation of some methylethyl ketone as well; some methylethyl ketone appears to be formed but its amount is extremely small. In the case of butene-1, small amounts of methylethyl ketone besides the main addition products, 1,2-epoxybutane and *n*-butanal, indicate that minor addition to the *more*-substituted carbon atom of the double bond might be also taking place. The same is true for propylene where small amounts of acetone seem to be formed, besides the expected main addition products, propylene oxide and propanal. With tetramethyl ethylene the addition products are tetramethyl ethylene oxide and pinacolone, as expected.

The case of *cis*-pentene-2 is of particular interest since it shows that in terms of the above rules the carbon atom to which the methyl radical is attached is "*less* substituted" than the other carbon atom of the double bond to which an ethyl radical is attached. Addition of an oxygen atom to the former would lead to the formation of methyl-*n*-propyl ketone besides 2-methylbutanal and the two isomeric epoxides, *cis*- and *trans*-2,3-epoxypentane, while the addition to the latter would result in diethylketone and the same

aldehyde and epoxides. Methyl-*n*-propyl ketone is definitely the predominant ketone formed although, perhaps, small amounts of diethylketone are formed as well.

Cycloölefins represent an interesting special case. For cyclohexene, for example, the same reaction scheme would require the formation of the following compounds:



C VII VIII IX

In addition to cyclohexene oxide (VII), two carbonyl compounds would be expected to be formed: cyclohexanone (VIII) through migration of an H atom and cyclopentyl formaldehyde (IX) through migration of the "radical" attached to the carbon atom to which oxygen is attached in the biradical (C). These compounds are actually formed and no other products have been detected.*

There are indications that the intermediate biradical (B) is very short-lived. This is suggested by the difference in the ratios of *cis*- and *trans*-2,3-epoxybutane formed in the reactions of oxygen atoms with *cis*- and *trans*-butene-2, respectively. The lack of appreciable effects of the presence of molecular oxygen on the amounts of the addition products formed also supports this conclusion. It appears, therefore, that the initially formed biradical isomerizes extremely rapidly into the final addition compounds. Since these reactions, however, are very exothermic, the addition compounds carry a large excess of energy when formed (carbonyl compounds about 115 kcal./mole and epoxides probably about 90 kcal./mole). The probability of decomposition of these compounds before dissipation of the excess energy can take place will depend largely on their complexity (the number of "degrees of freedom"). The simplest olefin, ethylene, appears to undergo almost exclusive decomposition on reacting with oxygen atoms. Propylene exhibits a pronounced collisional stabilization of the addition products formed (Fig. 1), while pressure effects appear to be absent with higher alkenes in the investigated pressure range. There is, however, a certain amount of decomposition even when no pressure effects are observed, which suggests that there is an intrinsic probability of a certain fraction of the initially formed biradical undergoing fragmentation. In view of the extremely short life of the biradical, it is not surprising that this fragmentation process is pressure independent.

The nature of the two types of fragmentation processes occurring in the reactions of oxygen atoms with olefins should now be briefly discussed. The pressure-dependent fragmentation, as observed in the case of propylene (and previously with ethylene), is characterized by the formation of products which could be expected from thermal decomposition of the major addition products and is consistent with the assumption that these are initially formed in an energy-rich state. The excess energy is in most cases readily removed by collisions in the gas phase. An inspection of the data given in Tables II and IV shows that the initial act (or part of the initial act) of the pressure-independent decomposition is probably the splitting off of a radical attached to the same carbon atom to which oxygen initially adds. In other words, the same particles which migrate in the rearrangement processes may become detached from the molecule.

**Details of the experiments performed with cyclohexene and cyclopentene will be published elsewhere.*

Thus, ethane is formed only in those cases where CH_3 is a migrating particle and then a great part of the resulting product is inhibited by the additions of O_2. The remaining fraction of the molecule would probably dimerize and the amount of the dimer formed should be comparable with that of ethane. Such dimers are likely to be of too low volatility to be readily detectable by the analytical techniques employed. Their formation could explain the low material balances observed. The pressure-independent fragmentation in the case of butene-2 appears, therefore, to be similar to the pressure-independent decomposition induced in 2,3-epoxybutane by mercury photosensitization (10). It is not certain whether migrating H atoms split off to a small extent. Thus, in the case of *iso*-butene, in spite of considerable effort no products other than the addition products already described could be isolated and identified. Any free H atoms which might be produced by splitting off from the initially formed biradical would readily add to excess *iso*-butene and the tertiary butyl radicals formed would be largely converted to compounds of low volatility.

The data in Fig. 1 for the propylene reaction can be treated kinetically. Thus, a plot of the reciprocal rates of the production of propanal (plus small amounts of acetone) against reciprocal pressure gives a straight line (Fig. 2), indicating a single-stage collisional

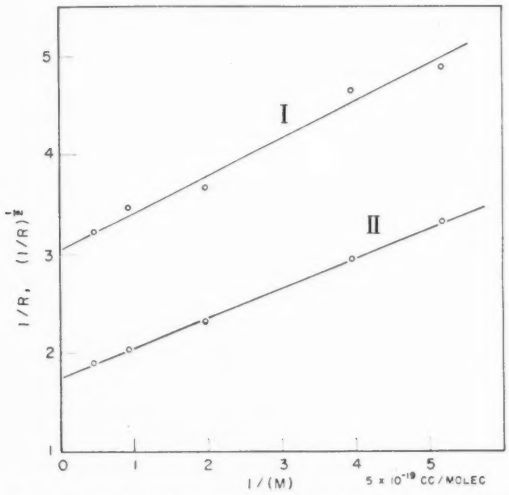


FIG. 2. I. Plot of the reciprocal relative rate ($1/R$) of formation of propanal + acetone against the reciprocal concentration of reactants. II. Plot of the square root of the relative rate of formation of propylene oxide $(1/R)^{\frac{1}{2}}$ against the reciprocal concentration of reactants.

deactivation. A similar plot for propylene oxide shows a distinct curvature; a plot of the square root of the reciprocal rate against reciprocal pressure, on the other hand, is a straight line. Such a relationship should be expected for a two-stage collisional deactivation with decomposition occurring at both stages provided the lifetimes of the two forms are approximately equal. The following reaction scheme for the propylene reaction is probably, with minor modifications, representative of the general reaction scheme for the reactions of oxygen atoms with olefins, provided it is realized that with increasing number of degrees of freedom the energy-rich molecules formed become longer lived and the pressure-dependent fragmentation becomes less important under otherwise comparable conditions.

$$C_3H_6 + O \rightarrow CH_3 \cdot \dot{C}H - CH_2O. \rightleftarrows \begin{cases} C_2H_5CHO^* & [1] \\ CH_3CH-CH_2^{**} \ (\diagdown O \diagup) & [2] \end{cases}$$

$$\text{decomposition} \qquad [3]$$

$$C_2H_5CHO^* \rightarrow \text{decomposition} \qquad [1a]$$

$$C_2H_5CHO^* + M \rightarrow C_2H_5CHO + M \qquad [1b]$$

$$CH_3CH-CH_2^{**} \ (\diagdown O \diagup) \rightarrow \text{decomposition} \qquad [2a]$$

$$CH_3CH-CH_2^{**} \ (\diagdown O \diagup) + M \rightarrow CH_3CH-CH_2^{*} \ (\diagdown O \diagup) + M \qquad [2b]$$

$$CH_3CH-CH_2^{*} \ (\diagdown O \diagup) \rightarrow \text{decomposition} \qquad [2c]$$

$$CH_3CH-CH_2^{*} \ (\diagdown O \diagup) + M \rightarrow CH_3CH-CH_2 \ (\diagdown O \diagup) + M \qquad [2d]$$

If, as assumed, $k_{2a}/k_{2b} = k_{2c}/k_{2d}$, the steady-state treatment leads to the relationships

$$1/R_{1b} = (1/\alpha_1)(1+k_{1a}/k_{1b}(M))$$

and

$$(1/R_{2d})^{\frac{1}{2}} = [1/(\alpha_2)]^{\frac{1}{2}}(1+k_{2a}/k_{2b}(M)),$$

where R_{1b} and R_{2d} are the rates of production of propanal and propene oxide per oxygen atom consumed, and α_1 and α_2 are the fractions of O atoms consumed in reactions (1) and (2) respectively. Taking approximately $k_{1b} = k_{2b} = k_{2d} = 10^{-10}$ cc./molec. sec., the plots in Fig. 2 indicate that the lifetimes of the energy-rich molecules $C_2H_5CHO^*$, $CH_3.CH-CH_2^{**}$ ($\diagdown O \diagup$), and $CH_3.CH-CH_2^{*}$ ($\diagdown O \diagup$) are between 10^{-8} and 10^{-9} second. It ought to be stressed, however, that the good straight-line plots in Fig. 2 are considerably better than should be expected in view of the likely experimental errors, and their quantitative implications should be taken with some reserve. Reaction (3) in the above scheme represents the pressure-independent fragmentation process.

The chemical reactions of oxygen atoms with olefins and the molecular rearrangements following the initial addition of the atoms exhibit certain regularities which have to be considered in the light of hyperconjugation and inductive effects. These regularities embrace: (1) systematic variation of reaction rates with the structure of the olefin, (2) specificity with respect to the position of addition of the atoms, and (3) nature of internal rearrangements which take place. These effects can best be discussed simultaneously and it is, therefore, convenient to defer their discussion until further results of the present investigations are published, particularly the relative rate constants of these reactions.

Oxygen atoms produced by the technique employed in the present study are probably in their ground, $O(^3P)$ state. This conclusion is valid provided the spin conservation rule is obeyed in the mercury-photosensitized decomposition of nitrous oxide. In this connection it is of interest that investigations now carried out in this laboratory (11) show that the course of the reaction of butene-1 with $O(^3P)$ atoms produced by photolysis of NO_2 is the same as observed in the present work.

ACKNOWLEDGMENTS

The author is indebted to Mr. L. C. Doyle for valuable assistance in the experimental work reported, to Dr. A. W. Tickner for mass spectrometer analyses, and to the Analytical Section of this Division for the infrared analyses.

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STUDIES OF THE MECHANISM OF THE FORMATION AND DECOMPOSITION OF THE MOLECULAR COMPLEX BETWEEN SOLID UREA AND *n*-OCTANE VAPOR[1]

H. G. McAdie[2] and G. B. Frost

ABSTRACT

The formation and decomposition of the molecular complex between solid urea and *n*-octane vapor, in the presence and absence of initiators, has been studied by a variety of techniques. Suggestions are made for the possible mechanism of this heterophase reaction incorporating known structural and thermodynamic data.

INTRODUCTION

It has been known for some time that when straight-chain hydrocarbon molecules are added to a concentrated solution of urea in a suitable solvent, crystallization of the urea molecules occurs in such a way that each hydrocarbon molecule becomes imprisoned in a canal formed by a hexagonal lattice of urea molecules, as contrasted with the normal tetragonal lattice of urea.

Schlenk (1) has reported that a slow formation of such molecular-inclusion complexes (frequently referred to as adducts) occurs on the mere contact of finely divided tetragonal urea crystals with certain pure liquid *n*-paraffins. Calderbank and Nikolov (2) have presented evidence that complex formation under these conditions is observable only when the particle size is less than a certain critical value.

Very little information is available regarding the formation of molecular complexes between solid (tetragonal) urea and *n*-paraffin vapor. Schlenk (1) noted that such a process could occur in air saturated with *n*-paraffin vapor if the *n*-paraffin possessed a relatively low boiling point. This type of reaction is of interest not only from the standpoint of the mechanism of complex formation under these conditions, but also since, in a more general way, it is an example of the type of heterophase reaction

$$\text{solid I} + \text{gas} \rightarrow \text{solid II}$$

for which a good deal of information is available regarding the crystallographic and energetic factors involved, and for which the changes occur in a readily accessible temperature range.

McAdie and Frost (3) attempted to carry out the process

$$\text{urea (tetragonal)} + n\text{-octane (vapor)} \rightarrow \text{complex (hexagonal)}$$

by exposing small urea crystals to *n*-octane vapor at close to its saturation vapor pressure at 25° C. for long periods of time, and were unable to observe any reaction. They found, however, that an uptake of the hydrocarbon occurred rapidly in the presence of water vapor; that if the products, so formed, were decomposed under vacuum, addition of *n*-octane then occurred rapidly in the absence of water vapor; and that cycles of decomposition and absorption of *n*-octane could then be carried out. The purpose of this paper is to report the results of some experiments which were designed to investigate these findings more extensively, and to consider the results in the light of the structural and thermodynamic data available. The experiments involve measurements of the rate of

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formation of the complex under various conditions in the presence and absence of water vapor, the identification of the lattice types by X-ray diffraction, the determination of changes in surface area, the effect of temperature, and other factors.

EXPERIMENTAL METHODS

Rate Studies

The apparatus is shown schematically in Fig. 1. Liquid *n*-octane was contained in a reservoir, R, the pressure of *n*-octane vapor being controlled by means of a jacket surrounding the reservoir through which water at any desired temperature could be

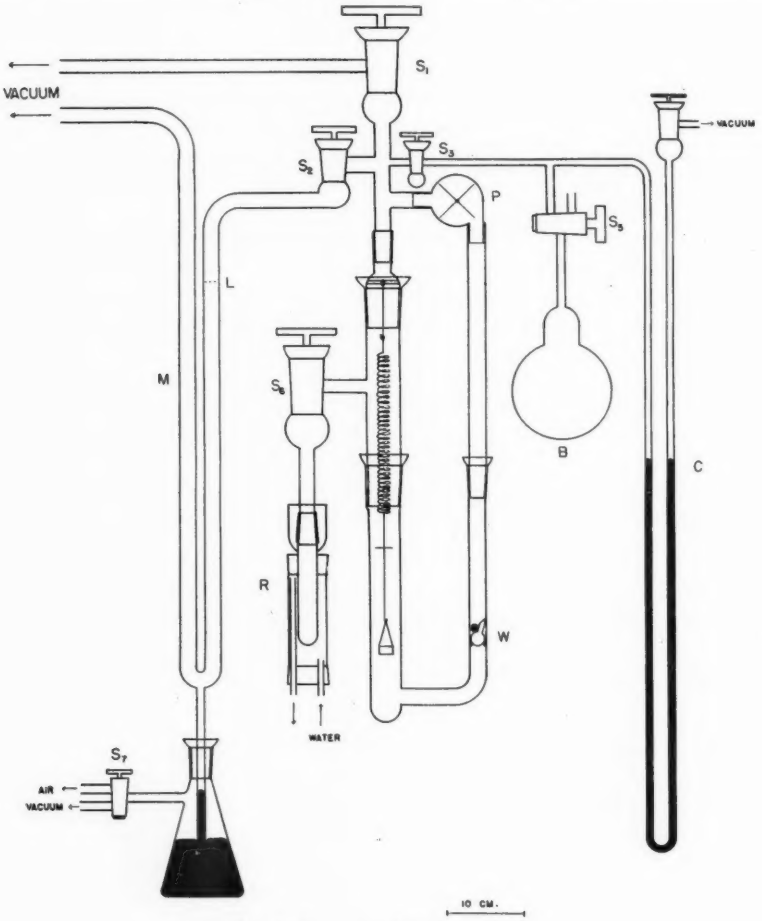

FIG. 1. Apparatus for rate studies.

rapidly circulated. Water vapor was introduced into the system by breaking a small bulb, W, containing the requisite amount of pure liquid water. The total volume of the reaction system to mark L on manometer M was found by application of the gas law in the usual way, making use of bulb B, which was of known volume, and manometer C.

To ensure mixing of the two vapors, a magnetically driven circulating pump, P, was provided. The entire apparatus was contained in a thermostatically controlled cabinet.

Reagent grade urea was recrystallized, dried, and screened, the "through 60 mesh on 80 mesh" portion being used. About 40 mg. of this material was weighed into a small copper gauze basket and suspended from a quartz spiral microbalance of sensitivity 2.006 mg. per mm. extension. The previously filled water bulb, together with a small steel ball for breaking, was placed in position. About 5 cc. of liquid *n*-octane was placed in reservoir R, with the constant-temperature jacket removed, frozen by means of liquid air, and repeatedly outgassed in the usual manner. Stopcock S_6 was then closed and the water jacket placed in position. The *n*-octane was brought to constant temperature by circulating water through the jacket. The cabinet was closed and brought to temperature.

After the urea was evacuated for 2 hours, the length of the spiral was measured to ± 0.01 mm. with a rigidly mounted twin telescope cathetometer and S_1 closed. The gas circulating pump, P, was started and S_6 opened to admit *n*-octane vapor to the system. The water bulb was broken and zero time for the reaction taken at this point. This was generally 1 to 2 minutes after the admission of the *n*-octane vapor.

Readings of spiral length, pressure on manometer M, and *n*-octane reservoir and cabinet temperatures were recorded at various intervals. The reaction was timed with an ordinary stopwatch.

When the reaction had proceeded to constant weight, S_6 was closed, S_1 opened, and the decomposition, under a pressure of 10^{-5} mm. Hg, allowed to proceed. S_6 was then carefully opened with S_1 still open and about 2 cc. of liquid *n*-octane evaporated in order to ensure removal of water vapor from the *n*-octane reservoir. S_6 was then closed and the system thoroughly evacuated. *n*-Octane was admitted to the system as described and the formation reaction in the presence of *n*-octane vapor only allowed to proceed. Subsequent decomposition and formation procedures were carried out in an identical manner.

X-Ray Diffraction Studies

Characterization, by X-ray diffraction, of the products formed during repeated formation and decomposition reactions was made by means of the apparatus shown in Fig. 2, in which the bulb below the stopcock S_3 contained water and that below S_2 contained liquid *n*-octane. This arrangement ensured adequate mixing of the vapors. A series of segments of urea were loaded into the long capillary tube, T, made of Corning 707-DG lead-free glass. After outgassing of the reactants, and evacuation of the urea for 24 hours, S_1 was closed and S_2 opened. When the equilibrium vapor pressure of *n*-octane was reached, as indicated by the manometer M, S_3 was opened until sufficient water vapor had been admitted. S_3 was then closed and reaction allowed to proceed. After 24 hours' exposure, one segment of urea was sealed off out of the center of the capillary and the X-ray diffraction pattern determined using copper K_α radiation. A central segment was chosen, so that if reaction were found to have occurred in this region, it was reasonable to assume that other segments of urea, through which the vapors had to pass before reacting with the segment in question, had reacted also. After exposure to vacuum for 24 hours at 25° C., with S_2 closed, a second segment was sealed off and its diffraction pattern determined. A similar procedure was followed after re-exposure to *n*-octane vapor only, for 24 hours, and also after re-evacuation for 24 hours.

The diffraction patterns obtained were compared with those obtained from tetragonal urea and from several known urea–*n*-paraffin complexes prepared from solution.

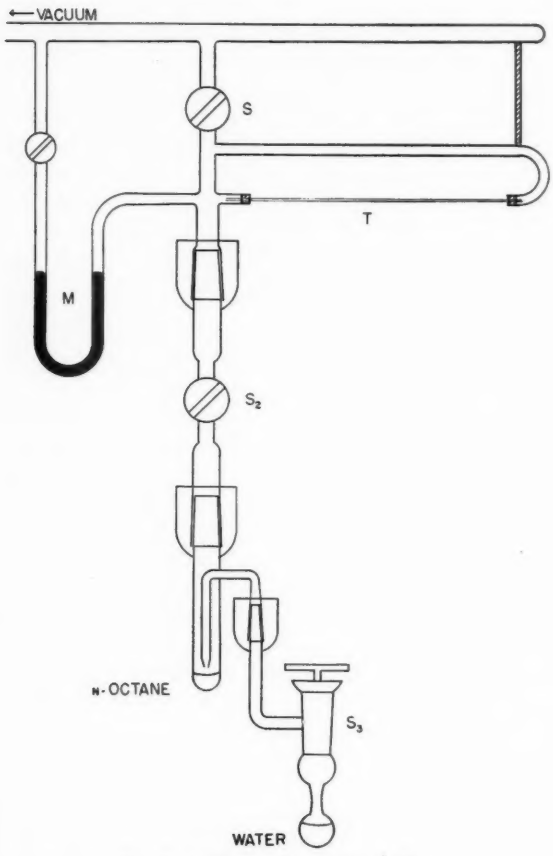

FIG. 2. Apparatus for X-ray studies.

Surface-Area Measurements

Measurements of the changes in surface area resulting from successive formation and decomposition reactions were obtained by argon adsorption at liquid-nitrogen temperatures in the usual volumetric manner. The adsorbent was contained in the annular space between two concentric cylinders of 100-mesh copper gauze. Following determination of the isotherm for urea of the particle size used in the rate experiments, the system was evacuated for 24 hours and subjected to *n*-octane and water vapors, the gas mixture being formed in an assembly similar to that shown in Fig. 2. The partial pressure of water vapor was 12.0 mm. and that of *n*-octane was 13.1 mm. The mixture was allowed to remain in contact with the urea for 5 days to ensure complete reaction. The system was then evacuated for 24 hours at room temperature (Residue I) and a second isotherm determined. The sample was exposed for 5 days to *n*-octane vapor only at its saturation pressure, the system evacuated for 24 hours (Residue II), and a third isotherm determined.

Photomicrography

Changes in the appearance of urea crystals during complex formation were followed by photomicrographic observation. Urea crystals were placed on a small glass plate ground smooth on both sides, the underside of which was painted with optical black to reduce reflections. The plate was contained in a glass tube connected to an assembly similar to that shown in Fig. 2, by means of which the urea crystals could be exposed to *n*-octane vapor and water vapor at known pressures. A small hole was blown out directly over the position of the plate, the edges ground, and a small clear glass plate cemented in position. The usual microscope and camera assembly were provided.

After evacuation of the urea for 2 hours, and outgassing of the *n*-octane and water reservoirs, the urea was photographed and exposed to a mixture of vapors. Photographs were then taken at regular intervals until the reaction was completed, as determined from earlier rate studies under identical conditions. Vacuum was then applied and the crystals photographed while undergoing decomposition.

RESULTS

Preliminary Rate Determinations

The results of a series of formation and decomposition reactions are shown in Fig. 3. These curves differ from those previously reported (3) in that diffusion effects were substantially eliminated by the gas circulating pump shown in Fig. 1. A sample of 0.0364 g. urea was exposed, at 25° C., to a mixture of *n*-octane and water vapor, the partial pressures being 13.1 mm. and 10.0 mm., respectively. An increase in weight was observed, the weight becoming constant in about 7 hours. The amount of *n*-octane taken

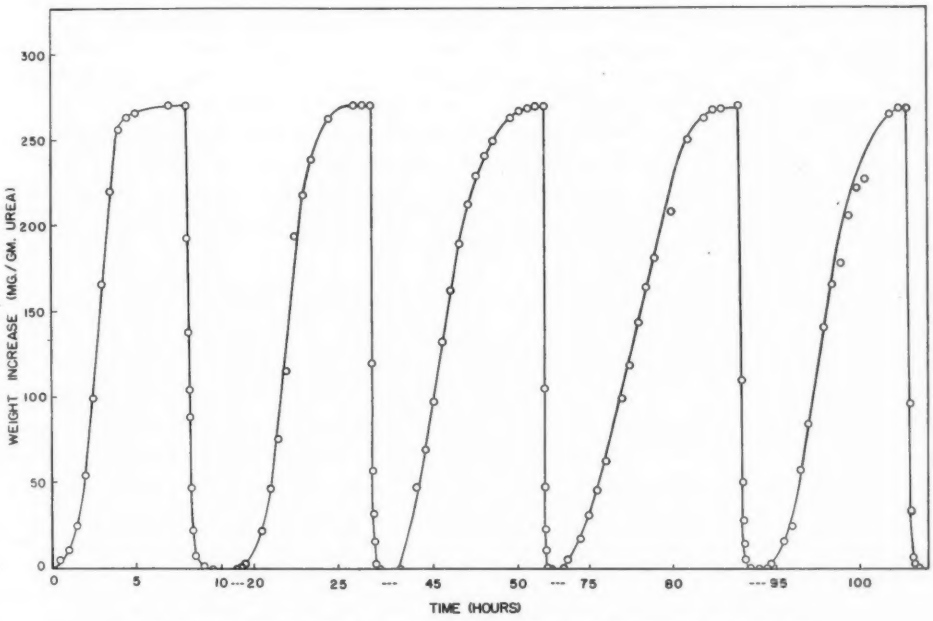

FIG. 3. Experimental results of successive formation and decomposition reactions.

up was found to be 272.3 mg. per g. urea. From the crystal structure data reported by Smith (4), the composition of the urea–*n*-octane complex is 272.7 mg. *n*-octane per g. urea. A marked swelling in the crystal mass was noted.

The system was evacuated, a rapid loss in weight being observed but no visible change in the volume of the crystal mass. The sample was next exposed to *n*-octane vapor only at 13.1 mm. pressure and an uptake of *n*-octane was observed, constant weight being attained at the same composition as before. Further decomposition and formation reactions were then carried out, no further change in the volume of the crystal mass being visible.

It is apparent that, although tetragonal urea of the particle size used is unreactive to *n*-octane vapor initially, absorption of the hydrocarbon does occur in the presence of water vapor, and that if the hydrocarbon is removed by evacuation, the residual urea is reactive to hydrocarbon and the presence of water vapor is unnecessary. The constancy of composition in successive formation reactions, and the agreement of these values with those reported by Smith (4), suggest that water is not retained in the complex in measurable amounts. From this it appears that the function of water vapor is merely to initiate the reaction.

The formation curves are all of the type characteristic of growth processes, an initial, gradual increase in rate being followed by a linear portion, this being followed in turn by a decline in rate as the reaction nears completion. No long induction periods were observed. The rate of formation, as indicated by the linear slopes of the formation curves, decreases with the number of times the reaction is carried out. It appears that the reaction proceeds to completion and is not impeded by formation of a surface layer of complex. The very rapid decomposition of the complex when subjected to vacuum, and the absence of induction periods under these conditions, are also of interest.

No change in spiral extension was observed when urea was exposed for long periods of time to water vapor only, at pressures comparable to that used in the foregoing experiment. Adsorption of water vapor at such pressures is, therefore, too small to be detected by the quartz spiral used. When the urea, so exposed to water vapor, was subjected to vacuum and then exposed to *n*-octane vapor, no reaction was observed. It is clear, therefore, that the urea crystals cannot be activated for complex formation by prior exposure to water vapor followed by evacuation, but that the reaction is initiated by water vapor in the presence of the hydrocarbon vapor.

X-Ray Diffraction Studies

The marked differences between the X-ray diffraction patterns of tetragonal urea and urea in the hexagonal complex lattice enabled the two lattices to be readily distinguished. Schlenk (1) has reported the similarity between the X-ray diffraction patterns of urea complexes of a given homologous series of reactant molecules. A number of urea–*n*-paraffin complexes, prepared from solution, confirmed this fact by giving identical diffraction patterns. All these patterns agreed with those obtained from the reaction products formed from tetragonal urea in the presence of *n*-octane vapor, with or without the presence of water vapor, thus confirming the presence of the hexagonal complex lattice. The diffraction patterns of the decomposition products formed by evacuation of the urea–*n*-octane complex conformed to that of tetragonal urea.

It is clear from these results that the complex is formed during exposure of urea to *n*-octane and water vapors, that on evacuation the lattice reverts to the tetragonal form, and that on subsequent exposure to *n*-octane vapor only, the complex is again formed, the lattice becoming hexagonal.

Surface-Area Measurements

The argon surface areas, calculated from Hüttig plots obtained from each isotherm, gave the following results:

Adsorbent	Area ($m.^2 g.^{-1}$)
Urea crystals	0.13
Residue I	1.76
Residue II	1.56

These values were found to be reproducible to about 10% although the absolute values given are not very significant in view of the relatively small areas involved. However, the 14-fold increase in the surface area of Residue I (obtained from formation of the complex in the presence of water vapor and subsequent decomposition) over that of the pure urea sample is of interest, as is the decrease in the area of Residue II (obtained by formation of the complex from Residue I in the presence of *n*-octane vapor only, and subsequent decomposition).

With successive formation and decomposition reactions, the decrease in surface area is attended by a corresponding decrease in the rate of reaction, as indicated by the slopes of the linear portions of the formation curves shown in Fig. 3. The ratio of the rates of complex formation with Residue I and Residue II is 1.32. The ratio of the corresponding surface areas is 1.13. The correlation is of interest bearing in mind the somewhat elaborate nature of the experiments and the sources of error attending them.

Photomicrography

Upon exposing urea crystals (following evacuation) to mixtures of *n*-octane vapor (about 13 mm.) and water vapor (about 16 mm.) the following observations were made:

(*a*) The reaction starts at random points, which are usually marked by the development of a slight protuberance of somewhat fuzzy appearance. The reaction spreads at first slowly and then quite rapidly through the crystal from these points.

(*b*) The time required for the initiation of the reaction is greater in some crystals than in others. The size of the crystal does not appear to be a significant factor.

(*c*) As the formation of the complex proceeds, the opaque appearance observed at the initiation of the reaction develops through the entire crystal.

(*d*) Essentially the same outward shapes of the original single crystals are retained during reaction, but some over-all expansion occurs, and the surfaces become very irregular and less clearly defined.

(*e*) No further visible change in shape or appearance occurs on evacuation, or on re-exposure to *n*-octane vapor only, although, as has been pointed out, X-ray diffraction shows that the hexagonal lattice is formed during reaction and reverts to tetragonal on evacuation.

Under the conditions of pressure employed, the reaction was complete in about 2 hours.

Effect of Water-Vapor Pressure on the Initial Formation Reaction

To determine the effect of water-vapor pressure on the rate of the initial formation of the complex, a number of experiments were performed at 25° C., using the apparatus shown in Fig. 1, at a pressure of 13.1 mm. *n*-octane. The pressures of water vapor ranged from 7.1 mm. to 16.3 mm.

A group of typical curves obtained are shown in Fig. 4. With decreasing pressure of water vapor, induction periods of increasing duration are observed, as well as decreasing slope of the linear portions of these curves. Rates, as estimated from these slopes, are

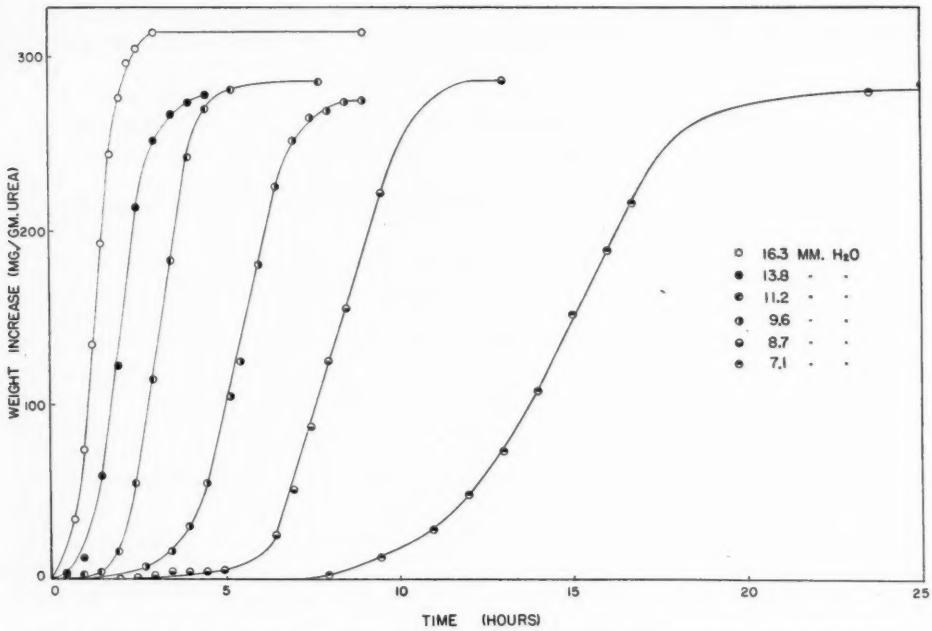

FIG. 4. Weight increase curves for constant *n*-octane pressure, constant temperature, and varying water-vapor pressure.

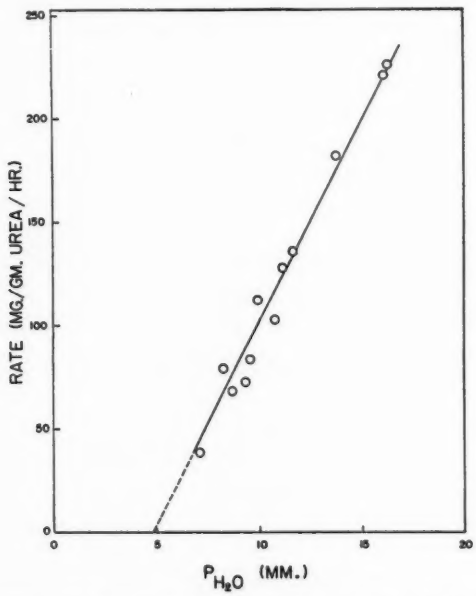

FIG. 5. Dependence of rate of initial formation reaction on water-vapor pressure.

plotted against the water-vapor pressure in Fig. 5. It will be seen that this rate is linearly dependent on the water-vapor pressure over the range of experiments. Extrapolation to zero rate suggests that a limiting pressure of 4.8 mm. of water vapor is required to initiate the complex formation reaction under these conditions. Separate experiments have shown that the reaction does not proceed at a measurable rate below this value.

The experiments at different pressures of water vapor were carried out using separate samples of urea. The composition of the end products obtained at water-vapor pressures of 11.2 mm. and 8.7 mm. is slightly higher than those shown in Fig. 3. These differences are probably due to errors inherent in the experimental method. The composition of the end product obtained at 16.3 mm. is significantly higher and may be due to adsorption of water vapor at this pressure, which is close to that of a saturated solution of urea in water.

Effect of n-Octane Pressure on the Initial Formation Reaction

A group of curves obtained at a constant water-vapor pressure of 11.5 mm., 25° C., and several *n*-octane pressures is shown in Fig. 6. The curves show the same features as those in Fig. 4, the slopes decreasing and the induction periods lengthening with decreasing *n*-octane pressure. Rates, as estimated from these slopes, are plotted against *n*-octane pressure in Fig. 7. This curve suggests that the reaction will not proceed below 7.2 mm. *n*-octane with the crystals of urea used in these experiments and in the presence of 11.5 mm. of water vapor at 25° C. A gradual leveling off in rate is observed as the *n*-octane pressure approaches the saturation pressure of 14.0 mm. at 25° C.

Effect of Temperature on the Initial Formation Reaction

A series of experiments were carried out at a constant *n*-octane pressure (9.8 mm.), a

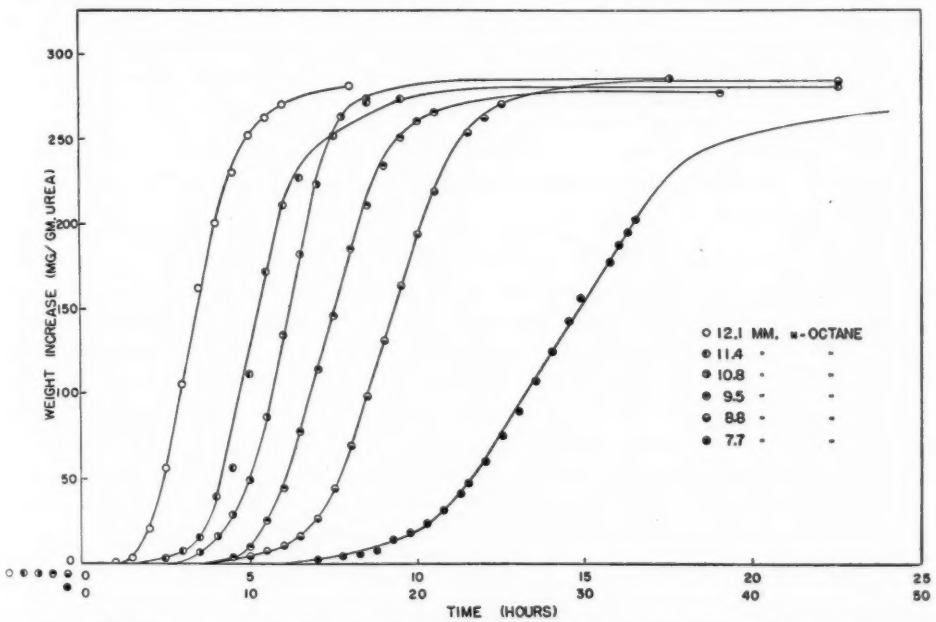

FIG. 6. Weight increase curves for constant water-vapor pressure, constant temperature, and varying *n*-octane pressure.

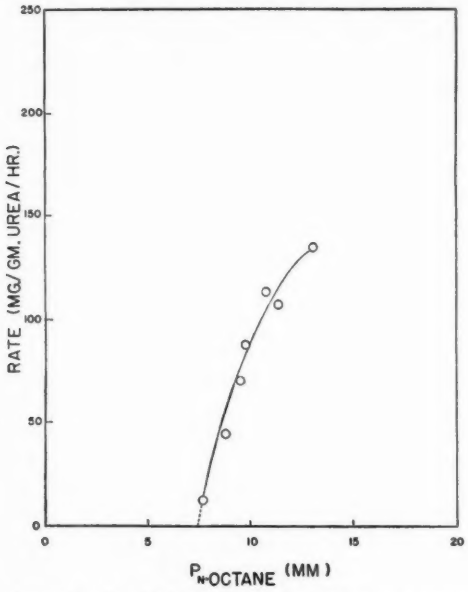

FIG. 7. Dependence of rate of initial formation reaction on *n*-octane vapor pressure.

constant water-vapor pressure (11.5 mm.), and different reaction temperatures. Weight increase versus time curves at 20.9° C., 22.4° C., and 25.0° C. are shown in Fig. 8. It will be seen that with increasing temperature over this range the induction periods lengthen markedly and the slopes of the linear portions of the curves decrease.

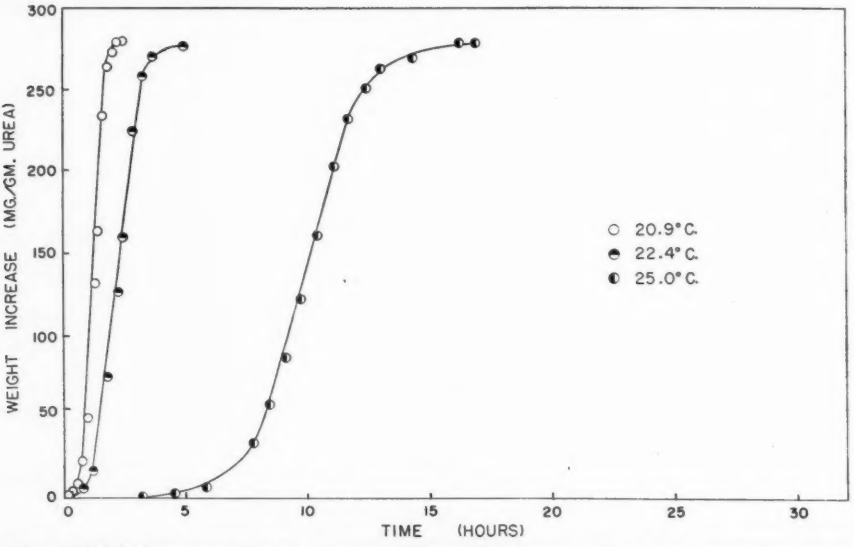

FIG. 8. Weight increase curves for constant water-vapor pressure, constant *n*-octane pressure, and varying temperature.

The dependence of rate, calculated from these slopes, on temperature is shown in Fig. 9. This indicates that under the particular experimental conditions employed, no reaction should be observed in finite time above 28.7° C. However, other conditions could conceivably alter this value.

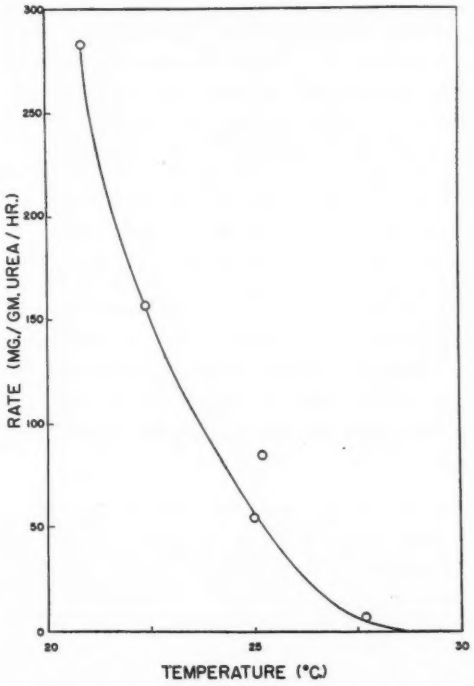

FIG. 9. Dependence of rate of initial formation reaction on temperature.

Effect of Temperature on the Second Formation Reaction

The effect of temperature on complex formation between *n*-octane vapor and the residue from a complex, previously formed in the presence of water vapor and decomposed, is shown in Fig. 10. Although the data are limited, it is significant that clearly marked induction periods are absent. However, the slopes of the linear portions of these curves decrease with temperature as in the case of the initial formation reaction.

Other Initiators

In view of the effect of water vapor in initiating the reaction between urea and *n*-octane vapor, a brief search was made for other compounds which might act in a similar manner. Two classes of compounds were considered, (*a*) those which were good solvents for urea, e.g. methanol and ethanol, and (*b*) those which are known to be highly polar e.g. nitromethane, ethylenediamine, and ammonia.

A small amount of urea, contained in a copper gauze basket, was exposed to *n*-octane vapor and the vapor of the particular compound being studied in an apparatus similar to that shown in Fig. 2. Swelling of the urea was taken as evidence of reaction, and X-ray diffraction patterns of the product were obtained as confirmation.

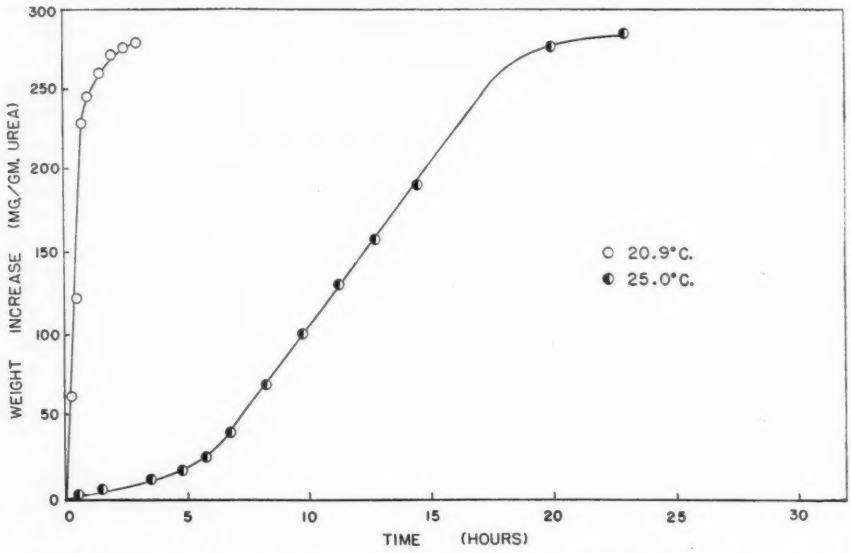

FIG. 10. Weight increase curves for the second formation reaction at constant *n*-octane pressure and varying temperature.

With methanol vapor at a pressure of about 12 mm., complex formation appeared complete after 12 hours. With ethanol vapor, at about 14 mm., about 48 hours were required. No reaction was evident with *n*-propanol vapor (10 mm.) after 1 week.

Reaction occurred in the presence of 12 mm. nitromethane vapor after about 80 hours, while with ethylenediamine at its saturation vapor pressure at room temperature, a slight swelling was observed after 5 days. No effect was found with ammonia.

In all cases, except with *n*-propanol and ammonia, X-ray diffraction patterns confirmed the presence of the hexagonal complex lattice.

DISCUSSION

Structural Factors

On the basis of X-ray (5, 6), infrared absorption (7), nuclear magnetic resonance (8, 9), and neutron-diffraction (10) data, the urea molecule may be said to possess an entirely planar structure.

The most careful determinations, by X-ray diffraction, of the crystal structures of tetragonal urea, and of urea in the hexagonal complex, have been carried out by Vaughan and Donohue (6) and by Smith (4), respectively. In the hexagonal complex, Smith (4) has shown that the molal ratio of urea to hydrocarbon is a linear function of the number of carbon atoms, n, in the hydrocarbon chain and is equal to $0.6848(n-1)+2.181$. Thus, 6.975 moles of urea are associated with 1 mole of *n*-octane in the urea–*n*-octane complex. Smith has also suggested that the configuration of the hydrocarbon molecules in the complex is very similar to that in the pure solid. Consideration of the crystal structure of these complexes shows that the hydrocarbon chains lie parallel to one another in the extended zigzag configuration.

Comparison of the tetragonal and hexagonal lattices of urea shows that the changes

in arrangement of the planar urea molecules occurring in the transition from the tetragonal to the hexagonal lattice involve the shortening of two N—H...O hydrogen bonds per urea molecule from a bond length of 2.99 Å to one of 2.93 Å. The two other N—H...O bonds per molecule of urea remain unchanged at a length of 3.04 Å. Data have recently been published on the heat of formation of N—H...O hydrogen bonds in various substances, obtained by subtracting the van der Waals energy from the total lattice energy as given by the heat of sublimation. Suzuki, Onishi, Koide, and Seki (11) suggest that the energies of N—H...O bonds will be greater in compounds where the ratio of the number of protons to the number of proton acceptors is unity, than in those compounds where it is greater than two. Examples of this latter class of compounds are urea, oxamide, and acetamide. From the data of Suzuki *et al.* (11) and the reported lengths of N—H...O bonds in oxamide (12), the heat of shortening of the N—H...O bond may be estimated to be 0.065 kcal. for a change of 0.01 Å. Thus, in the transition of urea from the tetragonal to hexagonal lattice, where two N—H...O bonds shorten by 0.06 Å each, the change in bond energy will be 0.78 kcal. mole^{-1} urea.

It has been suggested (4) that the van der Waals forces in tetragonal urea are less than normal because of the relatively open structure, while those in the complex appear to be normal. Because tetragonal urea possesses this relatively open structure, it would appear that in the tetragonal to hexagonal lattice transition there is a relaxation of the N—H...O hydrogen bond length to a state approaching the normal equilibrium distance, and not a compression of the bond to less than this distance. The process, therefore, should be exothermic, i.e. ΔH of shortening $= -0.78$ kcal. mole^{-1} urea for the tetragonal to hexagonal lattice transition.

Thermodynamic Considerations

Redlich, Gable, Dunlop, and Millar (13) have determined the equilibrium constants of a number of complex-forming reactions between urea and liquid hydrocarbons. The value of the equilibrium constant, K, corresponding to the standard free-energy change for the process

complex (hexagonal) → urea (tetragonal) + hydrocarbon (liquid)

is p/p_0, where p is the equilibrium pressure when the coexistent phases are complex, tetragonal urea, and hydrocarbon vapor, and p_0 is the vapor pressure of the pure liquid hydrocarbon. These workers reported, in graphic form, values of log p/p_0 for several hydrocarbons at various values of $1/T°$ K., the relations being found to be linear.

By interpolation from their data, and using the known values of the vapor pressure of liquid *n*-octane at various temperatures (14), values of the standard free-energy change corresponding to the change in state

urea (tetragonal) + *n*-octane (vapor) → complex (hexagonal)

have been calculated, and are given in Table I.

It is seen that this reaction, under standard conditions, becomes decreasingly spontaneous with temperature increase. From the data of Table I, there is obtained: $\Delta H°$ (over the temperature range) $= -20430$ cal. mole^{-1} *n*-octane; $\Delta S°_{298° \text{ K.}} = -58.07$ cal. deg.$^{-1}$ mole^{-1} *n*-octane. The process, therefore, is markedly exothermic, the enthalpy change being opposed by a large entropy factor. Also, it may readily be calculated that at 25° C. the complex will tend to form spontaneously at *n*-octane vapor pressures above approximately 4.0 mm.

Using the above data and the molal heats of vaporization and fusion of *n*-octane

TABLE I

STANDARD FREE-ENERGY CHANGE FOR THE PROCESS
urea (solid) + *n*-octane (vapor) → complex (solid)

T, ° K.	log p/p_0	p_0, mm.	p, atm.	$\Delta F°$, cal. mole^{-1} *n*-octane
273.16	−1.2329	2.86	0.00022	−4570
278.16	−1.0964	4.04	0.00043	−4290
283.16	−0.9518	5.63	0.00083	−3990
288.16	−0.8112	7.61	0.00155	−3710
293.16	−0.6667	10.46	0.00296	−3390
298.16	−0.5502	13.98	0.0052	−3120
303.16	−0.4257	18.45	0.0091	−2830
308.16	−0.3092	23.54	0.0152	−2560
313.16	−0.1928	31.11	0.0263	−2270

(9915 cal. mole^{-1} and 4957 cal. mole^{-1}, respectively (14)), it is found that for the process:

urea (tetragonal) + *n*-octane (solid) → complex (hexagonal)

$\Delta H°_{298} = -5560$ cal. mole^{-1} *n*-octane. However, it has been pointed out that 6.975 moles of urea are associated with 1 mole of *n*-octane in the complex; hence $\Delta H°_{298} = -800$ cal. mole^{-1} urea. This value agrees with the lattice energy change due to shortening of N—H...O bonds discussed earlier. Similar calculations for the complexes of *n*-decane, *n*-dodecane, and *n*-hexadecane give $\Delta H°_{298}$ values of −748, −750, and −720 cal. mole^{-1} urea, respectively.

This agreement suggests that the spontaneous energy liberation on complex formation is almost entirely due to the shortening of the N—H...O hydrogen bonds. In other words, the process of complex formation from tetragonal urea and *n*-octane vapor is energetically accounted for by this hydrogen-bond shortening along with the heat of solidification of gaseous *n*-octane. The configuration of the hydrocarbon molecules in the complex is similar to that in the pure solid hydrocarbon, and it appears, therefore, that any changes in the van der Waals forces between hydrocarbon chains lying parallel to one another in the solid state, and those lying parallel to one another in the hexagonal urea lattice, are not energetically significant. The process of complex formation appears, then, to involve a competition between the energetically favorable arrangement of planar urea molecules in a hexagonal lattice around the hydrocarbon molecule and a reversion to the more probable tetragonal configuration.

The Effect of Water Vapor

The foregoing experiments have shown that although complex formation is energetically favorable, actually no reaction is observed when small urea crystals are exposed to *n*-octane vapor only, at close to its saturation vapor pressure at 25° C. However, complex formation occurs in the presence of water vapor and if the complex so formed is decomposed under vacuum, addition of *n*-octane then occurs rapidly and cycles of decomposition and formation may be carried out.

The function of water vapor would appear to be the freeing of separate urea molecules from their positions in the tetragonal lattice. The lattice structure of urea suggests that on adsorption of water vapor on the crystal surface two types of hydrogen bonds may be formed, depending on the disposition of the urea molecules at the surface of the crystal, namely, N—H...O bonds between NH_2 groups and the oxygen of water, and O—H...O bonds between the C=O groups and the O—H of water. Since the O—H...O

bond is one of higher energy, the molecular field in the region of the adsorption interface will be disturbed, resulting in the weakening of the N—H...O bonds in the lattice itself. Severance of urea molecules may then occur under molecular forces comparable to those involved in the solution of urea in water. This severance may occur more readily at lattice imperfections. In the presence of hydrocarbon chains, which may be imagined as crystallization nuclei, the planar urea molecules so severed will "crystallize" in a hexagonal pattern around the hydrocarbon with the energetically favorable shortening of N—H...O bonds. Since water does not enter into the composition of the complex, it must be freed from the urea molecules in this process. As the interface spreads into the tetragonal crystal, the heat liberated by the exothermic reaction will aid in freeing an increasing number of urea molecules from their tetragonal environment. Photomicrographs have shown that the reaction proceeds from isolated points on the crystals, as would be expected if lattice imperfections are favorable points for nucleation.

The presence of a limiting pressure of water vapor below which the reaction is not observed suggests that a definite (although very small) amount of water must be adsorbed at the reaction sites in order to nucleate the process, that is to provide centers from which the exothermic reaction may proceed through the crystal. In this nucleation process the presence of both water and *n*-octane vapor is necessary. The curves of Fig. 4 and Fig. 6 show that the nucleation periods progressively shorten with increase in water-vapor pressure at a constant pressure of *n*-octane, or with increase in *n*-octane pressure at a constant pressure of water vapor. The rate of uptake of *n*-octane following nucleation increases with the pressure of water vapor (Fig. 4) or with the pressure of *n*-octane vapor (Fig. 6). These rates will depend upon the extent of nucleation, and possibly upon the rate of diffusion of *n*-octane and of water vapor into the reaction zone as the reaction interface spreads into the original crystal. From the data presented, it is not possible to separate these factors for quantitative discussion.

The Decomposition of the Complex under Vacuum

When the complex is formed in the presence of water vapor, a marked increase in the volume of the entire crystal aggregate is observed. Microscopic examination reveals also an over-all increase in the size of each individual crystalline unit, which might be expected since the volume of the hexagonal unit cell is greater than that of the tetragonal. Furthermore, the surfaces become very irregular, and the appearance becomes opaque.

When the complex is subjected to vacuum, rapid decomposition occurs, the lattice reverting to the tetragonal arrangement. It is interesting to note that this process occurs without induction periods (Fig. 3). This process may be analogous to the sublimation of a solid hydrocarbon, since essentially the same configuration exists for the hydrocarbon chain in the lattice of the complex as for such chains in the solid state (4). However, since the formation of the complex appears to involve a competition between the energetically favorable formation of the hexagonal lattice around the hydrocarbon mandrel, and a reversion to the more probable tetragonal configuration, a lowering of the density of hydrocarbon molecules below the equilibrium value would result in the collapse of the hexagonal lattice without the occurrence of a preliminary escape of the hydrocarbon molecules from the hexagonal canals. Regardless, however, of the mechanism involved, rapid reversion to the tetragonal form occurs. This should be attended by a decrease in volume. However, this does not occur. Photomicrographs show that the external size and appearance of the decomposed crystal is not significantly different from the complex crystal, although the surface may be more highly pitted. The surface area (1.76 $m.^2 g.^{-1}$) is about 14-fold that of the original urea crystals. This increase would be readily accounted

for by the observed irregularity of surface. It appears possible, therefore, that during the initial reaction a honeycomb structure of hydrocarbon molecules each surrounded by a hexagonal cage develops at the reaction interface and spreads through the entire crystal. The tendency toward lattice contraction upon reversion to the tetragonal form would set up severe strains causing some areas of the crystal to buckle. Alternatively, however, the development of an opaque appearance during the initial reaction may indicate that each of the relatively large crystals of tetragonal urea breaks down into a mosaic of microcrystals which together retain essentially the same outward shape as the original single crystal. On removal of the *n*-octane, the small crystals revert to the tetragonal form with individual contraction, but with little obvious change in what was the original crystal. The X-ray diffraction lines obtained after successive formation and decomposition reactions are more clearly defined than those obtained for the original urea crystals, which suggests that such microcrystals are formed. However, diffraction lines may be obtained for microcrystals as small as 100 Å in dimensions. On this view, the surface area should be very much greater than the value obtained. It is possible that the adsorbing gas measures only the external surface of the mosaic and not that of the individual crystals, which may lie very close together.

The Reaction in the Absence of Water Vapor

It is significant that the curves of Fig. 3 and those of Fig. 10 in comparison with those of Fig. 8 show that once the complex has been formed in the presence of water vapor and then decomposed, further formations occur without clearly marked induction periods. It follows that the tetragonal material formed by decomposition of the complex can reform the hexagonal complex without extensive nucleation. If decomposition of the complex results in lattice strain and buckling, such centers might well be points of attack where separate urea molecules would become separated for complex formation. On the other hand if a mosaic of microcrystals were formed, it is possible that a few of these are much smaller than 100 Å in size, and possibly of the order of a few unit cells. At such centers the molecular process of formation of the hexagonal lattice and reversion to the tetragonal can be readily visualized.

As the complex is formed and decomposed repeatedly, there will result a gradual ordering in the repacking of the urea molecules into the tetragonal lattice. This process has been shown to be attended by a decrease in surface area, and a corresponding decrease in rate. The correlation between rate and surface area may be simply due to the fact that there is a corresponding decrease in lattice imperfections or in extremely small and reactive microcrystals. However, the over-all reaction is exothermic and if this heat is a factor in energizing the urea molecules in the tetragonal lattice for complex formation it is obvious that the rate will increase as this heat can be utilized by a greater available surface.

Comment

Some preliminary experiments have been made on the adsorption of water vapor on urea crystals. These indicate the existence of a very small but definite adsorption, and of a monolayer formation in the region of water-vapor pressure (about 4 mm.) where nucleation is just observed. Further experiments are in progress from which it is hoped that accurate adsorption isotherms of water vapor and *n*-octane vapor on urea, and heats of adsorption, can be calculated. When the results of this and other work are available, it is hoped that it will be possible to assess the foregoing possible mechanisms in a more quantitative way, and to relate the effects of other initiators to those obtained with water vapor.

ACKNOWLEDGMENTS

The award of a Canadian Industries (1954) Limited Fellowship and a Research Council of Ontario Scholarship to one of us (H.G.M.) is gratefully acknowledged. Our thanks are due to the National Research Council of Canada, and to the McLaughlin Science Fund of Queen's University for financial support.

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A NEW SPOT TEST FOR NITRATE ION[1]

B. B. Coldwell and S. R. McLean

ABSTRACT

Under the influence of short ultraviolet radiation, diphenylamine and nitrate salts react to produce a yellow-colored product. The reaction appears specific and makes it possible to detect 1 μg. of nitrate ion in 0.01 ml. of solution.

INTRODUCTION

The well-known diphenylamine and brucine tests for nitrate (1), while sensitive, are lacking in specificity. Other oxidizing agents, such as chlorates and nitrites, give the same color reaction as nitrate (1, 2). In both tests the reagent is dissolved in concentrated sulphuric acid and this prevents their use for the detection of nitrate on substrates which might be charred by the strong acid, e.g. on paper chromatograms.

This paper describes a simple, specific, and relatively sensitive test for nitrate ion which does not require concentrated acid.

METHOD

The acidity of the test solution is adjusted with dilute sodium hydroxide or hydrochloric acid so that the pH lies between 3 and 10. A convenient volume (0.05 ml. to 0.01 ml.) is transferred with a pipette to a circle of No. 30 Whatman filter paper. The spot is allowed to dry at room temperature (or with gentle warming). The same volume of reagent (1% solution of reagent grade diphenylamine in absolute or 95% ethanol or methanol) is then spotted on either side of the test solution so that the areas covered by the reagent partially overlap the area occupied by the test solution. Alternatively, the reagent may be sprayed over the area of the test solution. After the solvent has evaporated, the filter paper is exposed to short-wavelength ultraviolet light for 2 to 5 minutes. If nitrate is present, the areas of the paper covered by both reagent and test solutions will show pale to bright yellow in daylight against the faint brown color of the area occupied by the reagent alone.

The *limit of identification* of the method was 1 μg. of nitrate ion and the *dilution limit* was 1:10,000.

While the *limit of identification* was found to be 1 μg., this quantity can be built up on the filter paper by successive application of more dilute solutions. Thus, nitrate was detected in a solution containing 0.2 μg. of the anion in 0.01 ml., by making five applications of this volume to the filter paper and allowing the spot to dry between the applications.

EXPERIMENTAL RESULTS

Interference of Cations and Anions

Preliminary tests established that the yellow color was given by all colorless solutions of nitrate salts. No cation interferences were observed. The test is unsatisfactory with highly colored solutions because the yellow color is usually obscure in these cases, e.g. with solutions containing relatively large amounts of iron, cobalt, copper, and cerium salts. Aqueous solutions of the following sodium or potassium salts gave no color with

[1]*Manuscript received December 6, 1957.*
Contribution from the Crime Detection Laboratories, Royal Canadian Mounted Police, Ottawa, Canada. Published with the permission of the Commissioner, R.C.M.P., Ottawa.

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diphenylamine under the conditions described above: acetate, bicarbonate, carbonate, chlorate, cyanide, thiocyanate, thiosulphate, sulphite, nitrite, chloride, iodide, "perborate", oxalate, mono- and di-hydrogen orthophosphate, sulphate, and hydroxide.

In Table I, the effect of various anions on the diphenylamine–nitrate reaction is summarized. It will be noted that only nitrite, bromate, iodate, and vanadate (ortho- and meta-) ions seriously affect the sensitivity of the reaction. Even in these instances

TABLE I

INTERFERENCE OF ANIONS WITH THE REACTION
(NO_3^- concentration = 5 μg./10^{-2} ml.)

Compound	Concn. of anion (μg./10^{-2} ml.)	Result*
NaCl	500	N.I.
KNO_2	30	S.I.
	15	N.I.
$KClO_3$	400	N.I.
NaCN	500	S.I.
	250	N.I.
Na_2CO_3	300	N.I.
$NaHCO_3$	300	N.I.
$NaHSO_4.H_2O$	1000	N.I.
$NaC_2H_3O_2.3H_2O$	500	S.I.
	250	N.I.
$Na_2S_2O_3.5H_2O$	1000	S.I.
	500	N.I.
$NaVO_3.4H_2O$	100	C.I.
	20	N.I.
$Na_3VO_4.16H_2O$	100	C.I.
	20	N.I.
NaCNS	1000	N.I.
NaI	1000	N.I.
Na_2SO_3	500	S.I.
	250	N.I.
$NaIO_3$	100	C.I.
	50	N.I.
$NaBO_3.4H_2O$	50	N.I.
$NaBrO_3$	125	C.I.
	60	N.I.
NaBr	1000	N.I.
NaOH	250	S.I.
	125	N.I.
$Na_2C_2O_4$	100	N.I.
NaF	100	N.I.
Na_2SO_4	1000	N.I.

*N.I. = *no interference, visible yellow color.*
S.I. = *slight interference, trace of yellow color.*
C.I. = *complete interference, no yellow color.*

5 μg. of nitrate ion can definitely be detected in the presence of 3 to 10 times this quantity of interfering ion. None of the compounds tested reacted with diphenylamine to give a color similar to that given by nitrates. Iodates and bromates gave a gray color, vanadates and peroxides a brown color, and mineral acids produced various shades of blue or green depending on the concentration. Nitrate was detected without difficulty in solutions made 0.1 *N* with respect to hydrobromic, molybdic, orthophosphoric, ortho- and hypo-phosphorous, hydrochloric, and sulphuric acids, in solutions containing penta- and tri-oxides of arsenic, and in sodium sulphide solutions. Thallous, stannous, and manganous ions did not interfere. If the solution was acidic, the yellow spot produced by the diphenylamine–nitrate reaction usually turned blue after several hours.

Effect of Other Factors

The ultraviolet light source used in these experiments was a Hanovia analytic model quartz lamp with type "L" burner,[2] which transmits radiations from 1849 Å into the visible spectrum. Test samples were prepared and exposed to the radiations passing the following filters:

Filter	Description*	Result
SC 5026	Range 3300–3900, maximum at 3600 Å	15 min. exposure—no yellow color
SC 5023	Range 3150–4100, maximum at 3660 Å	15 min. exposure—no yellow color
SC 5028 with SC 5025	Range 2300–4200, maximum at 3200 Å	2 min. exposure—yellow color

**Taken from transmission curves supplied by the manufacturer.*

Apparently, short-wave ultraviolet radiations are required to initiate the reaction between diphenylamine and nitrate resulting in the formation of a yellow product.

No yellow product was visible when the reaction was carried out on glass or porcelain plates. However, positive results were obtained when the reaction took place on glass wool, filter paper, or asbestos mats. Apparently the substrate is not involved in the reaction but may hinder or enhance visual detection of the yellow color. No characteristic colored product was observed when diphenylamine was replaced by diphenylbenzidine, diphenylnitrosamine, diphenylthiocarbazone, 1,3-diphenylguanidine, dipicrylamine, or brucine. α-Naphthylamine gave a yellow-orange to brown-colored product against a lilac-colored background.

Study of Yellow Substance

In the hope of characterizing the yellow-colored reaction products, large sheets of filter paper were soaked in aqueous 1% sodium nitrate solution, air-dried, and then treated with the diphenylamine reagent, air-dried, and exposed to ultraviolet light for approximately 5 minutes. Another lot of paper was treated with the reagent only and similarly exposed. In daylight, the latter had a very faint yellowish-brown tint compared to the bright yellow color of the nitrate-treated paper. Both lots of paper were extracted with ether. Drierite was added to each extract and after several days with intermittent shaking, the extracts were filtered and the filtrates concentrated to about 50 ml. The remaining ether was allowed to evaporate at room temperature and the residues were recrystallized from petroleum ether.

Microscopic examination of the products showed that the extract from the nitrate-treated paper consisted of crystals ranging in color from white through yellow to orange (product A), while the material extracted from paper treated only with diphenylamine consisted mostly of white and pale-yellow-colored crystals (product B). The melting point ranges of A, B, and diphenylamine were 49.9°–51.0° C.; 50.5°–51.5° C., and 52.5°–52.9° C., respectively. A minute orange-colored crystal from product A melted below 40° C. (All melting points are uncorrected.) Attempts to separate the yellow-colored material in product A from the rest of the mixture, by chromatographic methods, were unsuccessful.

The ultraviolet and infrared spectra of pure diphenylamine and products A and B were identical. At 397 mμ, A exhibited an absorption maximum, B gave some absorption but no pronounced maxima, while diphenylamine did not absorb (see Fig. 1).

The results suggest that diphenylamine undergoes a photochemical reaction when

[2]*Hanovia Chemical and Manufacturing Co., 100 Chestnut St., Newark 5, New Jersey.*

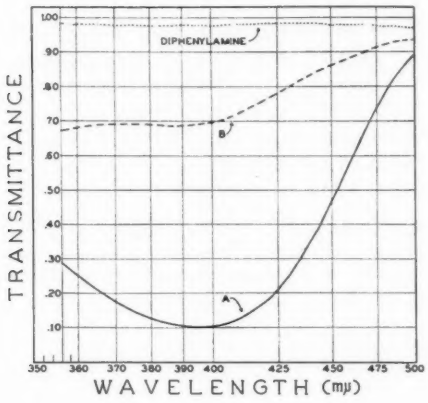

FIG. 1.

activated by short ultraviolet radiation to yield a yellow-colored product. Nitrate ions probably catalyze the reaction. The investigation is continuing.

SUMMARY

A new spot test for nitrate ion is described. The identification is based on the yellow-colored product formed when diphenylamine and nitrate, spotted on filter paper, are exposed to short-wave ultraviolet radiations. The yellow color is probably due to products formed during the photochemical reaction. The reaction appears specific and relatively sensitive, making it possible to detect 1 μg. of NO_3^- in 0.01 ml. of solution.

ACKNOWLEDGMENT

The authors are indebted to Mr. R. Lauzon for recording the infrared spectra.

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STRUCTURE AND PROPERTIES OF CYCLIC COMPOUNDS

XI. DISSOCIATION CONSTANTS OF THE CYANOHYDRINS OF SOME METHYLCYCLOHEXANONES[1,2]

OWEN H. WHEELER[3] AND JACOB Z. ZABICKY[4]

ABSTRACT

The dissociation constants of the cyanohydrins of a series of methylcyclohexanones have been measured. The polymethylcyclohexanone cyanohydrins show increasing instability on substitution owing to the effects of "axial crowding". The cyanohydrins of 3- and 4-methylcyclohexanone were found to be more stable than that of cyclohexanone and to explain this a new concept of "equatorial interference" is introduced.

The measurement of the dissociation constants of cyanohydrins has proved a useful method for studying the reactivities of aldehydes and ketones and has been used much (1, 2, 3, 4, 5).

As part of a general study of the effect of substitution on the reactivity of ring compounds we wished to investigate the influence of methyl groups, in various positions in the ring, on the reactivity of cyclohexanone. Accordingly, a series of methylcyclohexanones were prepared and the dissociation constants of their cyanohydrins measured (see Table I).

TABLE I

DISSOCIATION CONSTANTS OF THE CYANOHYDRINS

Cyclopentanone	149[a]	210[b]	205 ±6[c]	34.8[d]
Cyclohexanone	9.2	10	5.91±0.11	1.0
2-Methylcyclohexanone	5.9	—	10.7 ±0.3	1.8
3-Methylcyclohexanone	30	—	5.5 ±0.1	0.93
4-Methylcyclohexanone	12.7	—	3.15±0.05	0.53
2,2-Dimethylcyclohexanone	—	—	9.2 ±0.3	1.6
cis-3,5-Dimethylcyclohexanone	—	—	25.7 ±0.7	4.4
3,3-Dimethylcyclohexanone	—	—	176 ±4	30
3,3,5-Trimethylcyclohexanone	—	—	224 ±6	38
3,3,5,5-Tetramethylcyclohexanone	—	—	4690 ±120	800
Menthone	796	1300	313 ±11	53

[a]*In 96% ethanol at 20° ±0.5° (1).*
[b]*In 96% ethanol at 22°–23° (4).*
[c]*Present determinations, see Experimental.*
[d]*Ratio of dissociation constants to cyclohexanone cyanohydrin = 1.0.*

The cyanohydrin reaction has been shown to be reversible and to involve a base-catalyzed nucleophilic attack of cyanide ion on the carbon atom of the carbonyl group (6). The reaction involves a change in co-ordination number from 3 to 4 and Brown (7) has discussed such reactions in relation to the reactivity of simple cycloalkanones. Thus cyclopentanone is relatively unreactive in the cyanohydrin reaction (see Table I) since addition to the keto group gives a sterically crowded structure. However, cyclohexanone is much more reactive since a change to co-ordination number 4 relieves the angle strain in the ketone and also the small steric interference between the ketone group and the

[1]*Manuscript received November 7, 1957.*
Contribution from the Instituto de Quimica, Universidad Nacional Autonoma de Mexico, Mexico, 20, D.F. Part X, J. Org. Chem. **22**, *1153 (1957).*
[2]*A preliminary communication appeared in Chemistry and Industry, 1338 (1956).*
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adjacent hydrogen atoms (8). From the results in Table I it can be seen that the effect of placing methyl groups in the ring of cyclohexanone is to greatly reduce the stability of the cyanohydrins, except in the case of 3- and 4-methylcyclohexanone where there is a small but appreciable increase in stability.

Considering first the four dimethylcyclohexanones, the dissociation constant of 3,3-dimethylcyclohexanone cyanohydrin is much greater than either that of cyclohexanone or that of *cis*-3,5-dimethylcyclohexanone cyanohydrin. In the former case one of the methyl group must be in an axial position (9) and in the same axial direction as either a bulky cyano or a hydroxyl group. With the two large groups in this position there is considerable crowding in the cyanohydrin and consequently this readily dissociates to the ketone. This "axial crowding" effect of two bulky groups in the same axial direction is absent in *cis*-3,5-dimethylcyclohexanone cyanohydrin since both methyl groups lie in the equatorial plane (10). In the case of 2,2-dimethylcyclohexanone cyanohydrin one of the methyl groups will be in an axial position but in a direction opposite to the cyano group, and hence little "axial crowding" effect will be operative. However, the inductive effect of the methyl groups will place a partial negative charge on the carbonyl carbon atom and this will decrease the reactivity of the ketone (5) and increase the dissociation constant of the cyanohydrin. In menthone (2-isopropyl-5-methylcyclohexanone) the combined electronic and steric effects of the isopropyl group will make the cyanohydrin more unstable.

The cyanohydrin of 3,3,5-trimethylcyclohexanone is slightly less stable than that of 3,3-dimethylcyclohexanone since the extra methyl group will be in an equatorial position and exert only a small additional effect. However, in the case of 3,3,5,5-tetramethylcyclohexanone two methyl groups will be in an axial position and both in the same axial direction as the cyano (or hydroxyl) group. Consequently, there is a large "axial crowding" effect in the cyanohydrin, which is very unstable. The ratio of the stabilities of the cyanohydrins of cyclohexanone and cyclopentanone is 35:1 and the stabilities of most of the methylcyclohexanone cyanohydrins are within this range. However, in the cases of 3,3,5-tri- and 3,3,5,5-tetra-methylcyclohexanone the differences produced by the steric effects are equal to or greater than those which result from a difference in ring size.

Numerous examples exist in the literature of the instability of groups in an axial position (9) but few have demonstrated directly the presence of an "axial crowding" effect. Recently Corey and co-workers (11) have shown that while the preferred configuration of α-halogenocyclohexanones is with the halogen atoms axial, in the case of α-halogeno-4,4-dimethylcyclohexanones the halogen atoms are equatorial owing to crowding with the axial methyl group on carbon atom 4.

In the case of the monomethylcyclohexanones the 2-isomer will be subjected to the inductive effect of the methyl group, which will deactivate the ketone grouping and decrease the extent of cyanohydrin formation (5). The slightly increased reactivity of 2,2-dimethylcyclohexanone with respect to 2-methylcyclohexanone may be due to the fact that 2-methylcyclohexanone is free to assume both a methyl axial and an equatorial configuration (12) and the methyl group will have little steric effect on the ketone itself, whereas in 2,2-dimethylcyclohexanone one of the methyl groups will interfere with the ketone grouping (13) and this will favor the formation of the less-hindered staggered cyanohydrin. The cyanohydrins of both 3- and 4-methylcylcohexanone have dissociation constants which are smaller than that of cyclohexanone. The differences are not large, but are significant and suggest the operation of some other effect.

The large internal angle of the carbonyl group in cyclohexanone produces a twisting of the ring, and ring atoms 2 and 6 are pushed outwards and ring atom 4 turned inwards to the equatorial plane of the ring (8, 13). This brings the atoms on the equatorial bonds at positions 3 and 5 nearer to the equatorial bond of atom 4 and the axial bonds of atoms 2 and 6. This results in a general strain in the ring which is relieved when the co-ordination number of the carbonyl carbon atom is changed from 3 to 4 (7, 14) as in cyanohydrin formation. A substituent on carbon atom 4 will increase this strain relative to cyclohexanone itself and thus 4-methylcyclohexanone should be more reactive since the additional strain is relieved when the cyanohydrin is formed. In the case of 3-methylcyclohexanone the axial hydrogen atoms at positions 2 and 6 have some freedom of movement towards the carbonyl group and the effect will be less marked. The effect for which the term "equatorial interference" is suggested has not previously been noted. However, Brown, Fletcher, and Johannesen (14) found that in the hydrolysis of methyl-substituted 1-methyl-1-chlorocyclohexanes the order was 2-methyl > 3-methyl > 4-methyl, the reverse to that observed in the present work, and this would be expected since the reverse process of a change in co-ordination number from 4 to 3 is being measured. This distortion effect would be expected to be transferred into a second ring, and cholestan-3-one and coprostan-3-one have been found (15) to be slightly more reactive than cyclohexanone.

A quantitative comparison of the various non-bonded interactions must consider these effects in both the ketone and the cyanohydrin. Considering *cis*-3,5-dimethylcyclohexanone and 3,3,5-trimethylcyclohexanone and their cyanohydrins, interactions between the axial methyl groups and the axial hydrogen atoms will be present in both the ketones and their cyanohydrins. The principal factor contributing to the large difference between the dissociation constants of these cyanohydrins will be one non-bonded interaction between an axial methyl group and the axial cyano (or hydroxyl) group in the trimethyl ketone. The ratio of the two dissociation constants (8.7:1) gives a value of 1.3 kcal. (calculated from $\Delta F = -RT \ln(K_1/K_2)$ at 25.0°) for the free energy of interaction. Similarly the principal destabilizing effect contributing to the difference in stability of the cyanohydrins of *cis*-3,5-dimethyl- and 3,3,5,5-tetramethyl-cyclohexanone is two "non-bonded" axial interactions of methyl and cyano (or hydroxyl) groups, and the ratio of their dissociation constants (182:1) gives 1.55 kcal. for the mean interaction energy. The energy change on moving a methyl group from an axial to an equatorial position has been estimated to be about −1.8 kcal. (at 25°) (10) and found, from equilibration experiments on *cis*- and *trans*-dimethylcyclohexanes, to be about −1.5 kcal. (16). These are measurements of the repulsion energy between a methyl group in an axial position and the two hydrogen atoms in the same axial direction. Thus the individual methyl hydrogen interaction energy is about 0.8 kcal. From a study of the boric acid complexes of cyclohexanediols (17) the oxygen–oxygen axial–axial interaction energy is 1.9 kcal. The present results are thus reasonable in comparison with these other measurements.

The "equatorial interference" effect is much less than the "axial crowding" effect and in the case of 4-methylcyclohexanone increases the free energy with respect to cyclohexanone by −0.4 kcal. (ratio of dissociation constants 0.53:1). Small distortions resulting from "equatorial interference" will occur in the polymethylcyclohexanones but the effect is submerged by the much greater effects of "axial crowding". Nevertheless equatorial interactions cannot be ignored in any complete study of the influence of groups on ring reactivity, and further work is being carried out to test the hypothesis.

EXPERIMENTAL

Ketones

The ketones were initially fractionated and semicarbazones prepared from fractions of constant refractive index. The semicarbazones were recrystallized from ethanol or aqueous ethanol to constant melting point and the ketones liberated by steam distillation with phthalic anhydride (18). The regenerated ketones were carefully fractionated and middle cuts used for the equilibrium studies. The physical constants are given in Table II.

TABLE II

PHYSICAL PROPERTIES OF KETONES[a]

	Semicarbazone	B.p.[b]	n_D^{25}
Cyclopentanone	—	118°/580 mm. (129°/756 mm.)[c]	1.4328 (1.4368)[c,d]
Cyclohexanone	166° (165°)[c]	145°/580 mm. (155°/764 mm.)[c]	1.4482 (1.4498)[c,d]
2-Methylcyclohexanone	196.5° (196°)[c]	63° (165°/764 mm.)[c]	1.4449 (1.4477)[c,d]
3-Methylcyclohexanone	187.5° (191°)[c]	63° (169°/762 mm.)[c]	
4-Methylcyclohexanone	198° (197°)[c]	63° (170°/760 mm.)[c]	1.4412 (1.4457)[c,d]
2,2-Dimethylcyclohexanone	—	153°/580 mm. (169°/748 mm.)[c]	1.4453 (1.4490)[d,e]
cis-3,5-Dimethylcyclohexanone	—	151°/580 mm. (178°/760 mm.)[f]	1.4407 (1.4417)[d,f]
3,3-Dimethylcyclohexanone	210° (203°)[g]	80° (173°/750 mm.)[i]	1.4439
3,3,5-Trimethylcyclohexanone	201.5° (202°)[h]	90° (54°/11 mm.)[h]	1.4439 (1.4454)[h,i]
3,3,5,5-Tetramethylcyclohexanone	214.5° (217°–218°)[i]	95° (59°–61°/5.5 mm.)[j]	1.4509 (1.4520)[d,j]
Menthone	183° (183°)[k]	96° (98°–100°/18 mm.)[l]	1.4474

[a] *The figures in parentheses are the best literature values.*
[b] *At 23 mm. pressure, unless otherwise stated.*
[c] *Vogel, A. I. J. Chem. Soc. 1323 (1938).*
[d] n_D^{20}.
[e] *Cologne, J. and Duroux, E. Bull. soc. chim. France,* **7**, *459 (1940).*
[f] *Ungnade, H. E. and McLaren, A. D. J. Org. Chem.* **10**, *29 (1945); cf. Skita, A. and Faust, W. Ber.* **72**, *1127 (1939). They give* n_D^{20} *1.4466 for the trans-isomer.*
[g] *Blanc, H. G. Compt. rend.* **144**, *1356 (1907).*
[h] *Prizeheim, H. and Bondi, J. Ber.* **58**, *1409 (1925).*
[i] n_D^{15}.
[j] *Ref. 24.*
[k] *Neave, G. B. J. Chem. Soc.* **101**, *513 (1912).*
[l] *Ref. 20.*

Cyclopentanone, cyclohexanone, and 3- and 4-methylcyclohexanone were commercial samples (Eastman-Kodak white label grade).

2-Methylcyclohexanone and menthone were prepared by oxidation of the corresponding alcohols (19) and 2,2-dimethylcyclohexanone by methylation of 2-methylcyclohexanone (20).

cis-3,5-Dimethylcyclohexanone was obtained by hydrogenation of 3,5-dimethylcyclohexenone (21, 22) in ethanol over 5% palladium–charcoal and 3,3,5-trimethylcyclohexanone similarly from isophorone.

3,3-Dimethylcyclohexanone resulted from oxidation of 3,3-dimethylcyclohexanol (23) and 3,3,5,5-tetramethylcyclohexanone from a 1,4-addition of methylmagnesium iodide to isophorone (24).

Cyanohydrins

The solvent, 95% ethanol, was prepared by mixing 4 l. of lime-dried ethanol with 160 ml. of distilled water and had d_{25}^{25} 0.8020, d_4^{25} 0.7996.

Anhydrous hydrogen cyanide was prepared from sodium cyanide and 50% sulphuric acid (25) and dissolved in the above ethanol to give a *ca.* 0.1 *N* solution.

Aliquots of the pure ketone (0.015–0.15 g.) were dissolved in the 95% ethanol in a 50 ml. graduated flask and the hydrogen cyanide solution (10–20 ml.) added and 1 ml.

of a 2% solution of tri-*n*-propylamine in 95% ethanol. The solutions were allowed to reach equilibrium during 20–24 hours in a constant-temperature bath maintained at 25.0° ±0.2°. Samples (four of 10 ml.) were withdrawn and added to an excess of 0.1 *N* aqueous silver nitrate containing 0.5% nitric acid and the excess determined with standard 0.1 *N* potassium thiocyanate using ferric alum as indicator. All the determinations were carried out three to five times and the results, together with their mean standard deviations, are given in Table I.

The present results, obtained with highly purified specimens of ketones, differ from previous results obtained with ketones which have only been distilled.

ACKNOWLEDGMENT

The authors are grateful to the Rockefeller Foundation, New York, for financial assistance.

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HYDROGENOLYSIS OF CARBOHYDRATES

IV. 1,2-*O*-*ISO*PROPYLIDENE-D-GLUCOFURANOSE[1]

P. A. J. GORIN AND A. S. PERLIN

ABSTRACT

1,2-*O*-*Iso*propylidene-D-glucofuranose was treated with hydrogen at 180° C. and 2900 p.s.i. using copper chromium oxide catalyst and dioxane as solvent. The major isolated products were a hexanediol (2.4%), a mixture of hexanetriols (6.5%), a hexanetetrol (4.3%), and an *iso*propylidene-aldohexose (4.2%) which differed from the starting material. The latter product yielded L-idose on hydrolysis, showing clearly that isomerization of carbon 5 of monoacetone-D-glucose occurs under the reaction conditions used.

The diol and the major components of the triol mixture were found to possess a 1,2-glycol group which was derived mainly from the 5,6-glycol group of the original monoacetone-D-glucose. Thus, hydrogenolysis of 1,2-*O*-*iso*propylidene-D-glucofuranose-1-C^{14} afforded the 1,2-hexanediol and mixed triols containing only about 30% of the total specific activity in carbon 1. The tetrol was shown to be 1,2,5,6-hexanetetrol. The results suggest that the carbon–oxygen bonds at carbons 5 and 6 of *iso*propylidene-D-glucose are least prone to hydrogenolysis and that those at carbons 3 and 4 are most readily cleaved.

When methyl glycosides are subjected to hydrogenolysis in the presence of copper chromium oxide catalyst one of the major reactions involves reductive cleavage of the carbon–oxygen bond at the anomeric center with formation of an anhydro derivative (1, 2, 3). Thus methyl-β-L-arabopyranoside is attacked primarily at carbon–oxygen bonds 1, and 2 or 4, giving a mixture of 1,5-anhydro-2- and -4-deoxypentitols (*cis*- and *trans*-pyran-2,3-diols) (1). Likewise, methyl-α-D-glucopyranoside yields mainly a mixture of 1,5-anhydrodeoxyhexitols (2, 3). Sugar derivatives other than glycosides are now being examined to evaluate the stability of various substituent groups to hydrogenolysis, one objective being the possible discovery of resistant-blocking groups or of substituents easily cleaved, which may facilitate the preparation of deoxy sugars. The present paper concerns the hydrogenolysis of one of these derivatives, 1,2-*O*-*iso*propylidene-D-glucofuranose.

Under reaction conditions slightly milder than used earlier for the methyl glycosides, i.e., at about 180° C., at hydrogen pressures of 2000–3000 p.s.i., and with dioxane as solvent, the *iso*propylidene group was found to be more stable than a glycosidic methoxyl group, over half of the starting material remaining unchanged; no reaction occurred at 150° C., and at 250° C. extensive hydrogenolysis was evident. Among the reaction products obtained at 180° C. a sugar other than D-glucose was detected after hydrolytic removal of the *iso*propylidene groups. This sugar was isolated in 4.2% yield by cellulose-column chromatography (4) as a levorotatory sirup ($[\alpha]_D$ −10°) which formed a crystalline 1-benzyl-1-phenylhydrazone. The rate of movement of the sugar on a paper chromatogram (R_F = xylose) suggested that the compound might be deoxy-hexose. However, treatment of the sugar with 1.5 moles of lead tetraacetate in acetic acid and hydrolysis of the resulting formate esters gave two products which were indistinguishable from xylose and threose on a paper chromatogram. Since under the same conditions D-glucose gives D-arabinose and D-erythrose (5), it was evident that the configuration of the

[1]*Manuscript received January 2, 1958.*
Contribution from the National Research Council of Canada, Prairie Regional Laboratory, Saskatoon, Saskatchewan. Presented at the 132nd Meeting of the American Chemical Society, New York, N.Y., September, 1957. Release granted December 16, 1957.
Issued as N.R.C. No. 4651 and Paper No. 251 on the Uses of Plant Products.

hydroxyl group at carbon 5 of the D-glucose had been altered during the hydrogenation reaction. The sugar was shown, in fact, to be L-idose, for on treatment with phenylhydrazine acetate it yielded L-idose phenylosazone (L-sorbosazone) and on reduction followed by acetylation it gave L-iditol hexaacetate (6).

The conversion of D-glucose into L-idose affords a clear demonstration of a sugar isomerization promoted by catalytic hydrogenation conditions. Taken together with the recent finding (3) that dihydro-D-altral is formed from methyl-α-D-glucopyranoside and the observation (7) that under similar conditions D-xylose, D-ribose, and D- and L-lyxose are obtainable from methyl-β-L-arabopyranoside, the present results suggest that extensive isomerization may occur during hydrogenolysis reactions. Cyclic alcohols are known to isomerize in the presence of Raney nickel or platinum catalysts and hydrogen (8). It has been postulated that an intermediate ketone is formed in this reaction so that the over-all reaction represents a dehydrogenation followed by hydrogenation. A similar mechanism may be operative also in the current isomerizations of carbohydrates but, as yet, no evidence is forthcoming to support such a possibility. An apparent isomerization has recently been encountered in the catalytic hydrogenation of hexahydroxybenzene for preparation of inositols (9).

In addition to *iso*propylidene-L-idose, the hydrogenolysis of 1,2-*O*-*iso*propylidene-D-glucofuranose gave a mixture of hexanepolyols, comprising a diol, at least two triols, and a tetrol, in yields of 2.4%, 6.5%, and 4.3%, respectively, based on the weight of starting material. The tetrol, which was readily isolated from an aqueous solution after extraction of the other reaction products into chloroform, was crystalline and yielded a crystalline tetraacetate. When treated with periodate it consumed 2 moles of oxidant and liberated 2 moles of formaldehyde, but gave neither formic acid nor acetaldehyde. These properties served to characterize the tetrol as 1,2,5,6-hexanetetrol (3,4-dideoxyhexitol).

The diol and triol fractions, obtained from the chloroform extract, were separated by cellulose column chromatography. The diol, which yielded a crystalline bis-*p*-nitrobenzoate, was shown to be 1,2-hexanediol for it consumed 1 mole of periodate with production of 1 mole of formaldehyde. The sirupy triol fraction consumed almost 1 mole of oxidant and yielded close to 1 mole of formaldehyde, establishing the presence of a 1,2-diol group as a main structural feature of the triols present. Periodic acid oxidation of the triols followed by reduction with sodium borohydride (10) yielded a mixture of alcohols which could not be completely resolved into pure components via the derived *p*-nitrobenzoates. One apparently pure tris-*p*-nitrobenzoate was obtained in low yield on recrystallization from ethyl acetate. The resistance of its parent triol to periodate oxidation indicates either a 1,3,5- or a 1,3,6-hexanetriol structure, making this minor component the only hydrogenolysis product isolated which is not reconcilable with Adkins' β-hydrogenation rule (11). Because of the possibility that isomerization had occurred during formation of the various polyols, the configuration of the secondary hydroxyls cannot be assigned with certainty by reference to the parent compound, D-glucose.

The 1,2-glycol group of the diol and triols was derived principally from the 5,6-glycol group of the original D-glucose derivative. This was shown by hydrogenolysis of 1,2-*O*-*iso*propylidene-D-glucofuranose-1-C^{14}. The labelled diol and triols obtained from the latter compound were oxidized with periodate yielding formaldehyde (isolated as the dimedon derivative), which accounted for only 24% and 35%, respectively, of the

specific activity of the acetone-glucose-1-C^{14}. Further, when the diol was oxidized with the permanganate–periodate reagent (12), it yielded *n*-valeric acid possessing an activity which corresponded to 73% of that of the starting material; likewise, the mixture of pentanediols derived from the hexanetriol-C^{14} fraction by sodium periodate oxidation followed by sodium borohydride reduction accounted for 70% of the total activity. About three-quarters of the 1,2-glycol groups of the diol and triol originate from carbons 5 and 6 of the D-glucose and the remainder from carbons 1 and 2, implying that at least two different mechanisms operate in the hydrogenolysis of the *iso*propylidene group, one involving cleavage of ketal carbon–oxygen bonds, the other, of alcohol or the hemiacetal carbon–oxygen bonds.

It appears unlikely that the polyols are formed as a result of hydrolysis of the *iso*propylidene group (although the solvent was not rigorously dried, and water is a product of the reaction). This is suggested by hydrogenolysis control runs using hexitols (13), presumably the first products formed if the acetone group is hydrolyzed off, in which the variety of products was much greater than found in the present instance. The formation of these polyols is taken, rather, as an indication of the relative stability to hydrogenolysis of the various carbon–oxygen bonds in 1,2-*O*-*iso*propylidene-D-glucose. Accordingly, the bonds at carbons 3 and 4 are by far the least stable, while those at carbons 5 and 6 are most resistant to reductive cleavage. These relative stabilities may be altered substantially, however, by modification of the *iso*propylidene-D-glucose molecule. For example, the corresponding 3-*O*-methyl- and 6-deoxy-derivatives are unaffected by treatment under the same reaction conditions (13). Still other substituents at different positions may induce greater susceptibility to hydrogenolysis. The utilization of variations of this kind, it is anticipated, should extend the usefulness of catalytic hydrogenation in the synthesis of carbohydrate derivatives.

EXPERIMENTAL

Paper chromatography was carried out on Whatman No. 1 filter paper using *n*-butanol–ethanol–water (40:11:19 v/v) as solvent. Spray reagents used were *p*-anisidine hydrochloride in butanol (14), aniline oxalate (15), and ammoniacal silver nitrate (16). Melting points are uncorrected. Evaporations were carried out under reduced pressure. Optical rotations were measured at 27° C.

Radioactive samples were combusted and the specific activity of the carbon dioxide liberated was measured by the procedure of Buchanan and Nakao (17).

Hydrogenolysis of 1,2-O-Isopropylidene-D-glucofuranose-1-C^{14}

The *iso*propylidene-D-glucose-1-C^{14} (22.5 g.; 6.84 mμc./mM.) in dioxane (400 ml.) was hydrogenated at 2000–2900 p.s.i. for 6 hours at 180° C. using copper chromium oxide (6.0 g.) as catalyst. Removal of the catalyst and solvent left a colorless sirup, an aqueous solution of which was continuously extracted with chloroform.

1,2,5,6-Hexanetetrol

The aqueous solution which had been extracted with chloroform was evaporated, giving a sirup (2.0 g.) which crystallized from methanol–acetone. Two recrystallizations from the same solvent mixture gave a hexanetetrol (0.66 g.), m.p. 95°–97° C. and $[\alpha]_D$ 0° (*c*, 1.5, saturated borax) (1 dm. tube). Calculated for $C_6H_{14}O_4$: C, 47.98%; H, 9.40%. Found: C, 47.75%; H, 9.42%. The periodate equivalent, measured by the arsenite method (18), was 80 (calculated value, 75) and the formaldehyde equivalent, measured by the

chromotropic acid method (19), was 63 (calculated value, 75). No formic acid (20) or acetaldehyde (21) was formed.

Acetylated by the hot sodium acetate method the tetrol gave a tetraacetate which, after two recrystallizations from acetone – light petroleum (b.p. 60°–80° C.), had m.p. 76°–77° C. and $[\alpha]_D$ 0° (*c*, 5.5, $CHCl_3$) (1 dm. tube). Calculated for $C_{14}H_{22}O_8$: C, 52.82%; H, 6.97%. Found: C, 52.85%; H, 7.30%.

1,2-Hexanediol

The chloroform extract (above) was evaporated to a sirup, which was dissolved in hot ethyl acetate (100 ml.). On cooling, unchanged 1,2-*O*-*iso*propylidene-D-glucofuranose was deposited and the filtered mother liquor was evaporated to a sirup (6.2 g.). The latter was dissolved in 0.1 *N* sulphuric acid (50 cc.) and hydrolyzed at 100° C. for 1 hour. The acid was neutralized ($BaCO_3$), and the solution filtered and evaporated to give a sirup. Paper chromatographic examination indicated a mixture with R_F's corresponding to glucose and a deoxy-hexose (*p*-anisidine hydrochloride spray) and also a triol together with smaller amounts of diol (ammoniacal silver nitrate spray).

The mixture was fractionated on a cellulose column. Benzene–ethanol–water (500:50:1 v/v) eluted the diol, which was obtained as a mobile sirup, $[\alpha]_D$ −12° (*c*, 2.0, saturated borax), distilling at 160°–170° C. (air bath) at 1 mm., and having a specific activity of 9.28 mμc./mM. (calc. 10.2 mμc./mM.). Yield 290 mg. Calculated for $C_6H_{14}O_2$: C, 60.98%; H, 11.94%. Found: C, 60.40%; H, 12.14%. It had a periodate equivalent of 124 and a formaldehyde equivalent of 104. Calculated periodate and formaldehyde equivalents, 118. The product had an infrared spectrum identical with that of an authentic specimen (22).

The diol (67 mg.) was converted to the bis-*p*-nitrobenzoate, which after two recrystallizations from ethanol had m.p. 91°–93° C. Yield 67 mg. Racemic 1,2-hexanediol bis-*p*-nitrobenzoate has m.p. 101.5°–102.5° C. (22); the lower melting point of the current material may be due to the presence of mixed D- and L-forms or of one isomer, the diol being optically active. Calculated for $C_{20}H_{20}O_8N_2$: C, 57.69%; H, 4.84%. Found: C, 57.40%; H, 4.79%.

The diol (59 mg.) was oxidized with periodic acid (0.21 g.) in water (10 ml.), and the solution was then distilled into a solution of dimedon (0.50 g.) in 50 ml. of 0.15 *M* phosphate buffer of pH 7.0. The formaldehyde dimedon which formed was filtered off and twice recrystallized from ethanol; yield 21 mg., m.p. 190°–191° C., specific activity 0.78 mμc./mM., corresponding to an activity of 13.3 mμc./mM. for C-1. Calculated for $C_{17}H_{24}O_4$: C, 69.83%; H, 8.27%. Found: C, 70.05%; H, 8.31%.

The diol (75 mg.) was oxidized for 4 hours with a solution (150 ml.) containing potassium permanganate (14 mg.), sodium periodate (580 mg.), and potassium carbonate (183 mg.) (12), excess reagent being destroyed with sodium bisulphite and 0.1 *N* sulphuric acid. The clear solution was extracted continuously with ether and the resulting extract was neutralized with dilute sodium hydroxide and then evaporated to dryness. The residue was dissolved in water (1 ml.), ethanol (10 ml.) added, followed by *p*-bromophenacyl bromide (180 mg.). After being refluxed for 1 hour, the solution was evaporated to dryness and the product was recrystallized three times from aqueous ethanol. The product had m.p. 71° C., undepressed on admixture with *n*-valeric acid *p*-bromophenacyl ester, and a specific activity of 3.13 mμc./mM. corresponding to an activity of 40.5 mμc./mM. for C-1. Calculated for $C_{13}H_{15}O_3Br$: Br, 26.7%. Found: Br, 26.2%.

Hexanetriol Fraction

The triol fraction (0.89 g.) was eluted from the cellulose column by *n*-butanol; it had $[\alpha]_D$ −3° (*c*, 1.6, saturated borax) and a specific activity of 9.50 mμc./mM. (Calc. 10.2 mμc./mM.). Oxidation of the material with periodic acid indicated a periodate equivalent of 143 and a formaldehyde equivalent of 140.

The triol (224 mg.) was oxidized in water (10 ml.) containing periodic acid (500 mg.). After 15 minutes a slurry of barium carbonate was added to remove excess iodate and periodate and the solution was filtered. The filtrate was treated with sodium borohydride (200 mg.) and after 15 minutes the solution was acidified with dilute sulphuric acid, then continuously extracted with ether, and the extract was evaporated repeatedly with methanol to remove boric acid. A sirupy product (143 mg.) was obtained and a 55 mg. portion was converted to its *p*-nitrobenzoate by the same method as described previously. Two fractions were obtained after several fractional crystallizations from ethyl acetate and ethyl acetate – light petroleum (b.p. 50°–60° C.). The major portion (33 mg.) had m.p. 153°–156° C. (an authentic specimen of 1,5-pentanediol bis-*p*-nitrobenzoate prepared in the same way had m.p. 101°–103° C.) and an infrared spectrum similar to that of 1,5-pentanediol bis-*p*-nitrobenzoate. Calculated for $C_{19}H_{18}O_8N_2$: C, 56.71%; H, 4.51%. Found: C, 57.17%; H, 4.72%. The specific activity of the bis-*p*-nitrobenzoate was 2.11 mμc./mM. On the basis of the infrared spectrum and periodate oxidation data, the product possibly comprises a mixture of 1,5-pentanediol bis-*p*-nitrobenzoate and an impurity, thus indicating a 1,2,6-structure for the parent hexanetriol. The minor *p*-nitrobenzoate component (5 mg.) had m.p. 171°–173° C. and a tris-*p*-nitrobenzoate structure was indicated by the carbon and hydrogen microanalyses. Calculated for $C_{27}H_{23}O_{12}N_3$: C, 55.77%; H, 3.99%. Found: C, 55.49%; H, 3.93%.

L-*Idose*

Elution of the cellulose column with *n*-butanol one-quarter saturated with water gave a reducing sugar as a sirup (0.94 g.) with $[\alpha]_D$ −10° (*c*, 0.8, water). The sugar was oxidized with lead tetraacetate in acetic acid (5). After 2, 5, 10, and 30 minutes 2.02, 2.08, 2.12, and 2.14 moles/mole of reagent were consumed respectively. Oxidation of the sugar with 1.5 moles/mole of reagent gave a mixture, which, after removal of inorganic material from the solution and hydrolysis of the resulting formate esters, was indistinguishable from xylose and threose on a paper chromatogram.

The sugar (0.35 g.) was heated for 4 hours at 100° C. in an aqueous solution (20 ml.) containing phenylhydrazine (0.89 ml.) and acetic acid (1 ml.). On cooling, yellow crystals were deposited and were filtered off and recrystallized twice from methanol–benzene. The product (0.16 g.) had m.p. 170°–172° C. and $[\alpha]_D$ −13.8° (*c*, 1.0, pyridine–ethanol (1:1 v/v)) and was indistinguishable from L-sorbose phenylosazone (23) by its X-ray diffraction pattern and mixed melting point. Calculated for $C_{18}H_{22}O_4N_4$: C, 60.32%; H, 6.19%. Found: C, 60.51%; H, 6.09%.

The aldose (98 mg.) was refluxed for 15 minutes in a water (10 ml.) – ethanol (5 ml.) mixture containing 1-benzyl-1-phenylhydrazine hydrochloride (110 mg.). The solution was evaporated to a sirup which crystallized. Three recrystallizations from benzene – ethyl acetate afforded L-idose 1-benzyl-1-phenylhydrazone (104 mg.) having m.p. 113°–115° C. and $[\alpha]_D$ −19° (*c*, 1.2, ethanol). Calculated for $C_{19}H_{24}O_5N_2$: C, 63.32%; H, 6.71%. Found: C, 62.94%; H, 6.79%.

The aldose (140 mg.) was dissolved in a solution of sodium borohydride (100 mg.) in water (10 ml.). After 3 hours excess reagent was destroyed with acetic acid and the

solution then treated with Amberlite IR-120. The solution was evaporated to dryness and excess boric acid was removed by repeated evaporations of the product in methanol; yield, 126 mg., of which 104 mg. was acetylated at 100° C. in a mixture of acetic anhydride (2 ml.) and sodium acetate (0.2 g.) for 1 hour. The acetate crystallized from ethanol, and recrystallization from the same solvent gave a product (95 mg.) having m.p. 123°–124° C. and $[\alpha]_D$ −23° (*c*, 1.1, chloroform). An X-ray diffraction pattern and mixed melting point showed that the compound was L-iditol hexaacetate (6). Calculated for $C_{18}H_{26}O_{12}$: C, 49.77%; H, 6.03%. Found: C, 50.01%; H, 5.99%.

ACKNOWLEDGMENTS

The authors are grateful to the following for their assistance: Mr. J. A. Baignée for microanalyses, Mr. J. W. L. C. Christ for technical assistance, Mr. J. Dyck and Dr. A. C. Neish for specific activity estimations, Mr. T. M. Mallard for X-ray diffraction measurements, and Mr. G. B. Rennie for preparation of infrared spectra. Dr. A. C. Neish kindly supplied a sample of L-iditol hexaacetate.

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ÉTARD REACTION

I. ITS SCOPE AND LIMITATION WITH SUBSTITUTED TOLUENES[1]

OWEN H. WHEELER[2]

ABSTRACT

The scope and limitations of the Étard oxidation of substituted toluenes to substituted benzaldehydes by chromyl chloride have been studied. The conditions of the reaction were investigated and an improved method of performing it was developed.

INTRODUCTION

Though the chromyl chloride oxidation of toluenes to benzaldehydes was discovered by Étard in 1877 (1, 2) the reaction has been little used and no systematic study has been made of its potentialities. In connection with other work it was necessary to prepare a series of substituted benzaldehydes and this method seemed the most general and convenient. Accordingly a study of its scope and limitations for the conversion of substituted toluenes to substituted benzaldehydes was carried out.

The procedure used is to add a solution of chromyl chloride to a stirred solution of the toluene. The solvents usually used are carbon tetrachloride (3, 4, 5), carbon disulphide (6, 7, 8, 9), and chloroform. Carbon disulphide has the disadvantage of a low boiling point. The chloroform must be free from preservative alcohol and also was found to give troublesome emulsions during working up. In preliminary experiments the yields were little different with each solvent and carbon tetrachloride was therefore chosen as the general solvent for the study.

A complex is formed as intermediate in the reaction and this must be hydrolyzed under reducing conditions to prevent oxidation of the benzaldehyde to a benzoic acid. Saturated aqueous sodium sulphite (3) was the most convenient, but the aqueous solution must be well cooled and stirred during addition to prevent overoxidation. It has been recommended (3) that the complex be isolated by filtration and decomposed separately. This gives a purer product, since the complex contains no unreacted toluene, but the decomposition was found to be less easily controlled than when carried out with the complex suspended in the original solvent.

During the exothermic addition of chromyl chloride to the toluene, the initial dark red color of the solution becomes dark brown to black as the complex is slowly precipitated. These observations suggest that the initial step is the formation of a π- or σ-complex between the aromatic and chromyl chloride, which is followed by the formation of the true solid complex. (Spectroscopic evidence has been obtained for the rapid formation of a soluble complex (10).) It has been the usual practice to allow the reaction mixture to stand for a period of a few days (3, 11) to several weeks (4, 8) to allow complete separation of the complex. However, if sufficient time is allowed for formation of the physical complex, it should be possible to accelerate the second step of formation of the solid complex without harm to the aromatic nucleus, by heating the reaction mixture. This has been found to be the case and the reaction time can be considerably reduced by allowing the mixture to stand a short time and then refluxing it for several hours. Reaction times of 2 to 12 hours only are then required and this makes the reaction

[1]*Manuscript received December 16, 1957.*
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a very convenient one. If the reaction mixture is not initially cooled, or is heated too soon after the chromyl chloride is added, a vigorous or explosive reaction can occur.

To study the scope of the reaction with various toluenes the addition was carried out as usual and the mixture allowed to stand overnight. The product was isolated in the normal way and the aldehyde content estimated gravimetrically with 2,4-dinitrophenylhydrazine reagent. In the preparative experiments the mixture was refluxed for several hours before decomposition. The optimum conditions of reaction were generally not determined though enough data (Table I) were collected to predict them. In the case of *p*-iodotoluene the most suitable conditions are reported.

TABLE I

	Toluene	Temp.[a]	Time[b]	Yield[c]	Conversion[d]
I	*o*-Methyl	R.T.	o.n.	28	51
II	*m*-Methyl	R.T.	o.n.	32	50
III	*p*-Methyl	R.T.	o.n.	35	45
IV	*p*-Fluoro	R.T.	3 days	85	40
V	*o*-Chloro	R.T.	o.n.	79	19
VI	*o*-Chloro	Reflux	6 hr.	58	90
VII	*p*-Chloro	R.T.	2 hr.	100	0
VIII	*p*-Chloro	R.T.	3 days	86	36
IX	*p*-Chloro	Reflux	4 hr.	78	95
X	*o*-Bromo	Reflux	6 hr.	60	95
XI	*p*-Bromo	R.T.	o.n.	87	23
XII	*p*-Bromo	Reflux	6 hr.	85	92
XIII	*o*-Iodo	R.T.	3½ days	50	6
XIV	*o*-Iodo	Reflux	15 hr.	56	24
XV	*p*-Iodo	R.T.	o.n.	77	10
XVI	*p*-Iodo	R.T.	3 days	72	25
XVII	*p*-Iodo	R.T.	7 days	65	50
XVIII	*p*-Iodo	Reflux	4 hr.	90	42
XIX	*p*-Iodo	Reflux	10 hr.	83	85
XX	*o*-Nitro	Reflux	10 hr.	45	15
XXI	*p*-Nitro	Reflux	10 hr.	36	26
XXII	*p*-Methoxy	R.T.	o.n.	7	0
XXIII	*p*-Hydroxy	R.T.	o.n.	20	0
XXIV	*p*-Mercapto	R.T.	o.n.	50	0
XXV	*p*-Chloromethyl	R.T.	o.n.	32	10[e]
XXVI	*p*-Cyano	R.T.	o.n.	35	<5
XXVII	*p*-Cyano	R.T.	3 days	22	5[f]

[a]*R.T. denotes room temperature (22°–25°).*
[b]*o.n. denotes stirring overnight.*
[c]*Percentage yield of distillable product.*
[d]*Percentage of aldehyde in product.*
[e]*Derivative m.p. ca. 258°. p-Tolualdehyde 2,4-dinitrophenylhydrazone has m.p. 232.5°–234.5°, Ref. 22.*
[f]*Solid m.p. 211°–214°. p-Cyanobenzoic acid has m.p. 219°, Ref. 23.*

The three isomeric xylenes (I–III) all give tolualdehydes with oxidation of only one methyl group, as previously observed (3, 11), since the complex precipitates and further reaction is prevented. The yields and conversions are little different for all three. For the series *p*-fluoro-, *p*-chloro-, *p*-bromo-, and *p*-iodo-toluene (IV, VII, VIII, XI, XV, XVI, XVII) the yields decrease progressively for reaction at room temperature. Good conversions are obtained for *p*-chlorotoluene by refluxing for 4 hours (IX), whereas *p*-bromotoluene requires 6 hours (XII), and *p*-iodotoluene requires some 10 hours (XVIII, XIX). In these cases the yields of recovered product are all good (>80%) and the aromatic nucleus is not destroyed by prolonged refluxing. In the case of the ortho-halogenated toluenes the increasing size of the halogeno atom for the series chlorine, bromine, and iodine results in a considerably decreasing ease of oxidation (V, VI, X, XIII, XIV). Good

conversions can be obtained in the case of *o*-chloro- (V, VI) and *o*-bromo-toluene (X) by refluxing, but *o*-iodotoluene (XIII) is only oxidized very slowly, and prolonged reaction (XIV) tends to destroy the entire molecule.

p-Nitrotoluene is only slowly oxidized (XXI) and the ortho-isomer less so (XX). This must be due to the deactivating effect of a nitro group on an aromatic ring (12).

Of the other substituted toluenes investigated (XXII–XXVII), none of them gave any useful yield of a substituted benzaldehyde. Very little methoxytoluene (XXII) was recovered from its reaction with chromyl chloride. The major product was an undistillable polymer, and the chromyl chloride, which is a strong Lewis acid, must have caused polymerization. However, in the case of *p*-cresol (XXIII) and *p*-thiocresol (XXIV), though no aldehyde was formed, increased quantities of starting material could be recovered.

In the oxidation of *p*-chloromethyltoluene only some 30% of product could be obtained, but this analyzed for 10% of aldehyde. The 2,4-dinitrophenylhydrazone seemed to be that of *p*-chloromethylbenzaldehyde, since it had a higher melting point than that of *p*-tolualdehyde, the other possible product, suggesting that the methyl and not the chloromethyl group had been attacked.

p-Toluonitrile (XXVI, XXVII) was largely destroyed by reaction with chromyl chloride but a small amount of *p*-cyanobenzoic acid could be isolated.

In many cases the Étard reaction provides a simple and convenient one-step method of converting a toluene to a benzaldehyde. This gives better yields than the corresponding oxidations with manganese dioxide (3, 13) in sulphuric acid or electrolytically (3), and is simpler than the two-stage conversions of side-chain bromination and hydrolysis (14) and of oxidation with chromium trioxide in acetic anhydride followed by hydrolysis of the resulting diacetate (15).

EXPERIMENTAL

Chromyl Chloride

Chromyl chloride was a gift from the Mutual Chemical Division of the Allied Chemical Corporation, and was used as received.

Toluenes

Most of these were commercial samples, which were distilled before use. Some were made by a Sandmeyer reaction from the appropriate toluidines (16, 17).

p-Methoxytoluene

p-Cresol (21.6 g.) was dissolved in water (100 ml.) containing sodium hydroxide (8.3 g.). The mixture was cooled to 10° C. and methyl sulphate (27.0 g.) was added dropwise with stirring over 1/2 hour (18). The mixture was heated under reflux for 2 hours, cooled, diluted with water, and then extracted with ether. Isolation of the product gave 19.5 g. (80%), b.p. 163°–165° at 580 mm., n_D^{21} 1.5112 (lit. b.p. 175°–177° (19)).

p-Chloromethyltoluene

A mixture of toluene (70 g.), paraformaldehyde (6 g.), and pulverized zinc chloride (6 g.) was heated to 60°, and a stream of gaseous hydrogen chloride passed in (20) for 20 minutes. The product (25 g.) had b.p. 88°–90° at 18 mm.

Oxidations with Chromyl Chloride

In a typical experiment the toluene (1/10–1/5 mole) was dissolved in carbon tetrachloride (5–6 volumes). Chromyl chloride (0.21–0.42 mole) in an equal volume of carbon

tetrachloride was added slowly over 1 hour with stirring and external cooling in a bath of cold water so that the temperature never rose above 35°. Stirring was continued for another 2 hours and the mixture was then either allowed to stand at room temperature or refluxed with stirring for a number of hours. If the reaction is *not initially cooled* or if stirring is discontinued too soon, a *violent or explosive reaction* may take place. The reaction mixture was decomposed by pouring onto a stirred mixture of ice and saturated aqueous sodium sulphite solution. The use of insufficient ice or stirring may lead to overheating and overoxidation of the benzaldehyde to the benzoic acid. The organic layer was separated and the aqueous layer extracted several times with carbon tetrachloride. Extraction is sometimes made difficult by the precipitation of basic chromium salts, and these can best be removed by adding diluted (1:1) hydrochloric acid. The products were isolated by distillation and their content of benzaldehydes determined by treating a portion with 2,4-dinitrophenylhydrazine sulphate dissolved in aqueous methanol. The precipitates formed on warming were washed with water and cold methanol and dried at 100° before they were weighed.

p-Iodobenzaldehyde

A solution of *p*-iodotoluene (43.6 g., 0.2 mole) in carbon tetrachloride (150 ml.) was placed in a three-necked flask, immersed in ice-cold water. Chromyl chloride (65.2 g., 0.42 mole) in carbon tetrachloride (150 ml.) was allowed to run in dropwise, with good stirring, during 1 hour. The mixture was stirred at room temperature for a further 1 hour, and then heated slowly to reflux during another 1 hour. The mixture was stirred while refluxing for a further 20 hours. The cooled reaction mixture was poured slowly with vigorous stirring by hand onto sodium sulphite (60 g.) dissolved in water (300 ml.) containing ice (300 g.). Diluted (1:1) hydrochloric acid (100 ml.) was added to dissolve the basic chromium salts, and the organic layer separated and the aqueous layer extracted three times with portions of carbon tetrachloride. The combined organic solution was washed with water and dried. The residue left when the solvent was removed was distilled, giving the product, b.p. 145°–150° at 25 mm., m.p. 55°–65° (27.0–30.0 g., 58–64%). A forerun, b.p. 125°–130° at 25 mm. (3.5–5.0 g.) was largely unchanged *p*-iodotoluene. The *p*-iodobenzaldehyde can be recrystallized from aqueous ethanol to m.p. 75° (lit. m.p. 77°–78° (21)).

ACKNOWLEDGMENTS

The author is grateful to the Rockefeller Foundation, New York, for financial assistance and to the Mutual Chemical Division of the Allied Chemical and Dye Corporation, Baltimore, for generous gifts of chromyl chloride.

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SLURRY TITRATIONS OF UNSTABILIZED CELLULOSE NITRATE[1]

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ABSTRACT

Slurry titrations were performed on unstabilized cotton and wood cellulose nitrates. The results for total sulphate were compared with those from gravimetric, 24-hour, and zero hydrolysis methods. The agreement was best in the case of wood cellulose nitrates. The ester sulphate contents obtained were also compared with those from 24-hour and zero hydrolysis. The agreement was again best in the case of wood cellulose nitrates. It was shown that slurry titration for the determination of sulphate acid ester could be used for wood cellulose nitrates containing not less than 100% sulphate ester, the error being −2.7 to −11.9%. For cotton cellulose nitrates, the results were not satisfactory.

INTRODUCTION

Unstabilized cellulose acetate and cellulose nitrate contain a small amount of sulphate. It has been established by Malm *et al.* (1) that the sulphate in unstabilized cellulose acetate is in the form of a sulphate acid ester, RSO_4H. The form of the sulphate content of unstabilized cellulose nitrate has for many years been a subject of discussion.

In 1942, Kullgren (2) produced some evidence for the presence of a hemiester form, RSO_4H, by means of ion-exchange studies. A few years later, support for the existence of a sulphate ester was obtained by Reeve and Giddens (3), who studied the mechanism of stabilization of cellulose nitrate by ammonia. Later, Miles (4) summarized the work done on the determination of sulphate ester in cellulose nitrate by means of titration in acetone solution. Gagnon *et al.* (5) have shown that the sulphate ester in unstabilized cellulose nitrate can be determined by titration in water, or by analysis for calcium after ion exchange, or hydrolysis in acetone/water, or determination of sulphate after treatment with 50% alcohol.

Recently, the hydrolysis method for determining the sulphate acid ester was carefully studied (6). The object of the present work was to evaluate the slurry titration of unstabilized cellulose nitrate in water and to investigate the possibility of using this type of titration for determining the sulphate acid ester content of unstabilized cellulose nitrate.

EXPERIMENTAL

Cellulose Nitrate

The preparation of the unstabilized cotton and wood cellulose nitrates was described in a previous paper (7). The sulphate content of the cellulose nitrates was determined as barium sulphate, (8), and the nitrogen by the Devarda method. In the present work, the nitrogen contents of the unstabilized cotton and wood cellulose nitrates varied from 12.1 to 7.7% and from 11.8 to 7.3%, respectively.

Slurry Titration of Unstabilized Cellulose Nitrate

The unstabilized cellulose nitrates were washed continuously with distilled water as previously described (8) and then dried to about 50% water content by centrifuging (5). Duplicate samples of moist cellulose nitrate (about 2 g. dry weight for cotton and 3 g. for wood cellulose nitrate) were placed in a beaker and distilled water (200 ml.)

[1]*Manuscript received November 14, 1957.*
Contribution from the Department of Chemistry, Laval University, Quebec, Que., with financial assistance from the Defence Research Board of Canada.
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was added. The mixture was well stirred and the acidity determined by titration with 0.01 *N* potassium hydroxide using a Macbeth pH meter. Hydrolysis of the cellulose nitrate was minimized by completing the titration within 20 minutes.

In later experiments, the unstabilized cellulose nitrate obtained after centrifuging was ground with sand, so that the slurry titration could be completed within 10 minutes. "Ottawa sand"* (Standard, code 2170, 30 g.) was placed in a mortar and moist cellulose nitrate (3–5 g.) and distilled water (15–25 ml.) were added. The mixture was ground vigorously with a pestle for 10 minutes. The contents of the mortar were transferred to a beaker, the pestle and mortar washed with distilled water, and the combined washings added to the mixture in the beaker. The volume of solution was then made up to 200 ml. The change in the pH of the solution due to the presence of the sand was negligible. The mixture was well stirred and the acidity determined as before.

RESULTS AND DISCUSSION

Determination by Slurry Titration of the Total Sulphate Content of Cellulose Nitrate

Titration of unstabilized cellulose nitrate in the form of a slurry in water, when performed before hydrolysis of the nitrate begins, provides a measure of the total sulphate content. Unstabilized cellulose nitrate is thought to contain a sulphate acid ester, RSO_4H, free sulphuric acid, and possibly a very small amount of a neutral ester, R_2SO_4. The slurry titration gives the acidity due to these constituents.

In the present work, the slurry titer, expressed as milliliters 0.01 *N* potassium hydroxide, was converted to milliliters per gram of cellulose nitrate. The proportion of the slurry titer value due to sulphate acid ester can be calculated using the sulphate acid ester content obtained by the hydrolysis method (6). The portion of the slurry titer due to sulphate acid ester can be converted to sulphate, expressed as % H_2SO_4, by using 98 as the equivalent weight of the ester. An example serves to illustrate the calculations involved. For instance, a cotton cellulose nitrate was shown to contain 96% sulphate acid ester by the hydrolysis method (6). The slurry titer expressed as ml./g. was 8.90. Therefore the proportion of the latter value due to ester was 8.54 ml./g., i.e. $8.54 \times 0.01 \times 98 = 8.36$ mg. H_2SO_4 per gram of nitrocellulose, which was equivalent to 0.84% H_2SO_4. Assuming that the amount of neutral ester is negligible, the remainder of the slurry titer value, 0.36 ml./g., represents free sulphuric acid. Conversion of the latter value, using 49 as the equivalent weight, gives 0.02% H_2SO_4. Therefore the total sulphate content was 0.86% H_2SO_4. The gravimetric and slurry titration total sulphate contents of a series of cotton and wood cellulose nitrates are compared in Table I. The differences are shown statistically in Table II, together with the confidence limits for the differences, calculated by the method of Dean and Dixon (9). The precision of slurry titration total sulphates is given in Table III. The coefficients of variation by differences between duplicate results (10) for cotton and wood cellulose nitrates were 1.5 and 2.5, respectively. The slurry titration results show best agreement with the gravimetric values in the case of wood cellulose nitrates.

In cases where there was 100% sulphate acid ester present in the cellulose nitrate, the total sulphate content and the sulphate due to sulphate acid ester had the same value because of the absence of free sulphuric acid. Thus the total slurry titer represented the sulphate content due to sulphate acid ester and, using 98 only as the equivalent weight, could be converted to sulphate. For example, a wood cellulose nitrate was shown to contain 100% sulphate acid ester by the hydrolysis method (6). The slurry titer,

**General Chemical Co., New York, N.Y., U.S.A.*

expressed as ml./g., was 14.10, which was equivalent to 1.38% H_2SO_4. Four examples of slurry titration total sulphate values for cellulose nitrates containing 100% sulphate acid ester are given in Table I.

TABLE I

COMPARISON OF GRAVIMETRIC, 24-HOUR HYDROLYSIS, AND ZERO HYDROLYSIS WITH SLURRY TITRATION RESULTS FOR TOTAL SULPHATE

Expt. No.	Cotton cellulose nitrate		Wood cellulose nitrate	
	Total sulphate, % H_2SO_4		Total sulphate, % H_2SO_4	
	Grav.	Slurry	Grav.	Slurry
1	1.55	1.60	2.31	2.25*
2	0.95	0.86	2.13	2.00
3	0.89	0.89*	1.81	1.78*
4	0.85	0.82	1.79	1.68
5	0.81	0.74*	1.71	1.60
	24-hr. hydrol.	Slurry	24-hr. hydrol.	Slurry
1	1.84	1.82	2.18	2.00
2	1.42	1.49	2.11	2.07
3	1.30	1.36	2.01	1.88
4	0.98	0.89	1.64	1.68
5	0.94	0.85	1.65	1.60
	Zero hydrol.	Slurry	Zero hydrol.	Slurry
1	1.85	1.82	2.27	2.00
2	1.33	1.36	2.17	1.88
3	0.96	0.85	2.15	2.25
4	0.94	0.71	2.14	2.07
5	0.87	0.72	1.80	1.78

**100% ester content.*

The total sulphate values obtained from the 24-hour hydrolysis and slurry titers are compared in Table I. The differences are shown statistically in Table II. The coefficients of variation for cotton and wood cellulose nitrates were 2.8 and 1.0, and the Rank-correlation coefficients (11) +0.80 and +0.97, respectively. It is evident that there is good agreement between the sulphate values, especially in the case of wood cellulose nitrates.

TABLE II

DIFFERENCES BETWEEN TOTAL SULPHATES DETERMINED BY SLURRY TITRATION AND THOSE DETERMINED BY OTHER METHODS

Samples	Differences	Methods		
		Grav.	24-hr. hydrol.	Zero hydrol.
Cotton	Mean difference, %	−5.1	6.0	12.4
Wood	Mean difference, %	−3.2	5.6	5.1
Cotton	Standard deviation	10.8	4.2	8.2
Wood	Standard deviation	7.7	4.5	4.7
Cotton	95% Confidence limits	−5.1±7.5	6.0±2.8	12.4±5.7
Wood	95% Confidence limits	−3.2±5.4	5.6±3.1	5.1±3.3

Comparison of Slurry Titration and Zero Hydrolysis Total Sulphates

It has been shown recently (6) that cellulose nitrate can be titrated in 90% acetone/water solution with no hydrolysis of the sulphate acid ester occurring. Therefore zero hydrolysis and slurry titers should give the same results, expressed as milliliters 0.01 *N* potassium hydroxide per gram of cellulose nitrate. Results obtained by zero hydrolysis and slurry titrations for cotton and wood cellulose nitrates were compared. For instance,

for a wood cellulose nitrate the zero hydrolysis titer expressed as ml./g. was 14.51 and the slurry titer 14.13 ml./g. In general, there was good agreement between results, especially for wood cellulose nitrates.

The zero hydrolysis titers can be converted to total sulphate values by using sulphate acid ester contents obtained by the hydrolysis method (6) and the appropriate equivalent weights as mentioned for the slurry titration results. Total sulphate contents determined by zero hydrolysis and slurry titrations for cotton and wood cellulose nitrates are compared in Table I. The differences are shown in Table II. The coefficients of variation for cotton and wood cellulose nitrates were 6.1 and 3.2 and the Rank-correlation coefficients were +0.70 and +0.92, respectively. The precision of zero hydrolysis sulphate values is given in Table III. The Rank-correlation coefficients for cotton and wood cellulose nitrates were +0.99 and 0, respectively. It is evident that there was good agreement between zero hydrolysis and slurry titration results.

TABLE III

PRECISION OF TOTAL SULPHATE DETERMINATIONS ON DUPLICATE SAMPLES OF CELLULOSE NITRATES

Samples	Differences	Methods	
		Slurry	Zero hydrol.
Cotton	Mean difference, %	3.9	4.6
Wood	Mean difference, %	2.4	1.6
Cotton	Standard deviation	2.7	3.3
Wood	Standard deviation	4.4	1.3
Cotton	95% Confidence limits	3.9±1.9	4.6±3.3
Wood	95% Confidence limits	2.4±3.1	1.6±1.3

Total sulphates were calculated from zero hydrolysis titers of cellulose nitrates prepared by duplicate nitrations. The precision of the sulphate determinations decreased as expected. For cotton cellulose nitrate the mean difference was 11.3%, the standard deviation 12.5, and the 95% confidence limits were 11.3% ±4.8, and for wood cellulose nitrate the corresponding values were 11.1%, 7.0, and 11.1% ±8.4. Total sulphates were also calculated from slurry titers of samples prepared by duplicate nitrations but were not reproducible.

Comparison of Slurry Titration with 24-Hour Hydrolysis and Zero Hydrolysis Ester Sulphates

Ester sulphate values as determined by the hydrolysis method (6) can be compared with those calculated from slurry titration. Twenty-four hour hydrolysis and slurry titration ester sulphates are compared in Table IV. The differences are shown in Table V. The coefficients of variation for cotton and wood cellulose nitrates were 6.7 and 1.7, respectively. The precision of slurry titration ester sulphates is given in Table VI. The coefficients of variation for cotton and wood cellulose nitrates were 1.4 and 2.6 respectively.

Further comparison can be made between zero hydrolysis and slurry titration ester sulphates as shown for cotton and wood cellulose nitrates in Table IV. The differences are given in Table V. There is agreement but the best results were obtained with wood cellulose nitrates. The precision of the zero hydrolysis ester sulphates is mentioned in Table VI. It decreases markedly for results obtained from samples prepared by duplicate nitrations. For cotton cellulose nitrates, the mean difference was 15.2%, the standard deviation 9.2, and the 95% confidence limits were 15.2% ±10.9. The corresponding values for wood cellulose nitrates were 12.2%, 5.2, and 12.2% ±6.2.

TABLE IV

COMPARISON OF 24-HOUR HYDROLYSIS AND ZERO HYDROLYSIS WITH SLURRY TITRATION RESULTS FOR ESTER SULPHATE

Expt. No.	Cotton cellulose nitrate		Wood cellulose nitrate	
	Ester sulphate, % H_2SO_4		Ester sulphate, % H_2SO_4	
	24-hr. hydrol.	Slurry	24-hr. hydrol.	Slurry
1	1.42	1.52	2.31	2.25
2	0.91	0.83	2.27	2.05
3	0.89	0.89	1.98	1.92
4	0.85	0.67	1.77	1.67
5	0.81	0.74	1.76	1.68
	Zero hydrol.	Slurry	Zero hydrol.	Slurry
1	1.84	1.81	2.19	1.92
2	1.30	1.32	2.15	2.25
3	0.94	0.83	2.11	2.05
4	0.87	0.72	1.95	1.68
5	0.86	0.64	1.80	1.78

TABLE V

DIFFERENCES BETWEEN ESTER SULPHATES DETERMINED BY SLURRY TITRATION AND THOSE DETERMINED BY OTHER METHODS

Samples	Differences	Methods	
		24-hr. hydrolysis	Zero hydrolysis
Cotton	Mean difference, %	12.9	12.5
Wood	Mean difference, %	4.0	4.5
Cotton	Standard deviation	9.8	9.1
Wood	Standard deviation	2.6	4.7
Cotton	95% Confidence limits	12.9±6.3	12.5±6.3
Wood	95% Confidence limits	4.0±1.7	4.5±3.3
Cotton	Rank-correlation coeff.	0.85	0.74
Wood	Rank-correlation coeff.	0.95	0.95

TABLE VI

PRECISION OF ESTER SULPHATE DETERMINATIONS ON DUPLICATE SAMPLES OF CELLULOSE NITRATES

Samples	Differences	Methods	
		Slurry	Zero hydrolysis
Cotton	Mean difference, %	3.2	2.8
Wood	Mean difference, %	2.4	2.2
Cotton	Standard deviation	2.3	4.6
Wood	Standard deviation	4.5	2.2
Cotton	95% Confidence limits	3.2±1.1	2.8±4.6
Wood	95% Confidence limits	2.4±3.1	2.2±2.2

In general, the slurry titration results are better if obtained from wood instead of cotton cellulose nitrates. It seems that the physical form of the cellulose nitrate plays an important part in the degree of success with slurry titrations. Wood cellulose nitrate could be finely divided whereas the cotton cellulose nitrate fibers retained their thickness even after they were ground and stirred rapidly in water. The zero hydrolysis titer can be looked upon as a more reliable measure of acidity than the slurry titer, because titration of cellulose nitrate in 90% acetone/water solution presents less difficulty than a slurry titration in water.

When ester contents of cellulose nitrates determined by the hydrolysis method (6) are used to calculate total sulphate and ester sulphate values from slurry titration, the latter values compare favorably with those obtained directly by the hydrolysis method. Furthermore, slurry titration results are similar to those obtained from zero hydrolysis titrations. The fact that both slurry and zero hydrolysis results compare satisfactorily with those obtained by 24-hour hydrolysis is good evidence that the latter method is reliable.

Slurry Titration as a Method of Determining Sulphate Acid Ester in Cellulose Nitrate

Slurry titration should provide a direct method of determining sulphate acid ester in unstabilized cellulose nitrate when the sulphate content is solely in the form of sulphate acid ester. This is the case for unstabilized cellulose acetate (1), but not for unstabilized cellulose nitrate, which frequently contains some sulphate in the form of free sulphuric acid.

In the present work, several unstabilized cotton and wood cellulose nitrates containing 100% sulphate acid ester were prepared. Slurry titrations were performed on these samples. Using 98 for the equivalent weight of the sulphate acid ester, RSO_4H, the slurry titer was converted to sulphate and expressed as % H_2SO_4. The latter value represented the sulphate due to ester and was expressed as a percentage of the standard gravimetric sulphate. The per cent sulphate acid ester content thus obtained was compared to 100% (the ester content determined by the hydrolysis method, which was taken as a standard). It was found that sulphate acid ester contents determined in this way for cotton cellulose nitrates were too low. However, in the case of wood cellulose nitrates, there was better agreement; the mean difference was -7.3%, the standard deviation 5.2, and the 95% confidence limits were $-7.3\% \pm 4.6$.

The slurry titration cannot be used as a direct method for determining sulphate acid ester in cellulose nitrates which contain less than 100% ester.

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THE DECOMPOSITION OF NITROUS OXIDE AT LOW PRESSURES ON NICKEL OXIDE CATALYSTS[1]

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ABSTRACT

Heterogeneous decomposition of nitrous oxide at pressures between 10^{-5} and 10^{-4} mm. on nickel oxide and doped nickel oxide catalysts has been studied in the temperature range 350° to 500° C. Under most experimental conditions the reaction is first order in nitrous oxide. The observed activation energies are considerably smaller than those observed in previous work and are decreased on doping with Li_2O and increased on adding Cr_2O_3. The results are explained by assuming that changes in the steady-state surface coverage with chemisorbed oxygen affect strongly the heats of chemisorption and, therefore, also the activation energies of the primary reactions.

INTRODUCTION

The heterogeneous decomposition of nitrous oxide has received considerable attention in the past. Studies on metallic catalysts (1, 2, 3, 4) have led to the conclusion that the decomposition is first order with respect to nitrous oxide and that the rate is reduced by the presence of oxygen. The work on metallic oxide catalysts has produced a less clear picture of the reaction kinetics (5, 6, 7, 8). In general the reaction appears to be retarded by the presence of oxygen. Some workers find a first-order dependence on nitrous oxide although a variable order and dependence on catalyst composition have also been observed (6).

In recent years the reaction has assumed considerable importance in the study of the catalytic properties of semiconductor systems with the object of correlating the electrical and catalytic properties.

In view of the apparent complexity of this decomposition we decided that it would be profitable to study the reaction at very low pressures under conditions of small percentage decomposition in an attempt to eliminate to a very large extent the effect of the products of the reaction and any diffusion effects which might interfere with the reaction.

EXPERIMENTAL

The reaction was carried out in a flow system in which nitrous oxide was streamed over the flat surface of a disk of the catalyst material at pressures between 10^{-4} and 10^{-5} mm. Hg. The rate of flow of gas over the catalyst was sufficiently fast for the transfer of gas to the internal pore structure of the catalyst to be negligibly small compared with the total flow. The undecomposed nitrous oxide was condensed in liquid nitrogen and the pressure of the noncondensable products measured continuously with a thermionic ionization gauge.

Nitrous oxide was allowed to stream through a capillary from a 5-liter reservoir filled initially to about 10^{-1} mm. The gas emerging from the capillary impinged on the surface of the catalyst and was rapidly removed by condensation in a liquid nitrogen trap placed as close to the reacting system as possible. The products nitrogen and oxygen were removed by a mercury diffusion pump with a pumping speed of 20 l./sec. They were pumped to the ionization gauge which was in turn evacuated through a narrow

[1]*Manuscript received December 4, 1957.*
Contribution from the Division of Applied Chemistry, National Research Council, Ottawa, Canada.
Issued as N.R.C. No. 4655.

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glass tubing by a second mercury diffusion pump at a rate of 0.1 l./sec. Thus the pressure of the products was increased in the region of the ionization gauge by the ratio of the pumping speeds at the catalyst and at the ionization gauge. The pumping speed at the catalyst was about 2 l./sec.

The reactor was constructed from Pyrex glass with the exception of the vacuum envelope which was of silica. The general design of the reactor was similar to the one used by Crocker (9) in the study of decomposition reactions on single crystal planes. The inlet capillary was jacketed so that the incoming gas could be held at a different temperature from that of the catalyst. It was hoped that by doing this the effect of the temperature of the incoming gas could be studied, but this was found to be impossible because of the relatively large number of secondary collisions made by the molecules before they were removed from the reaction zone. Only about 10% of the collisions with the catalyst were the initial collisions of the incoming gas. The reactor was heated by an external furnace and the catalyst temperature was measured by a Pt–Pt–Rh thermocouple pressed against the back surface of the catalyst disk. Diagrams of the reaction system and the reactor are given in Figs. 1 and 2.

The nitrous oxide was purified by the usual triple distillation procedure and was stored in a 2-liter glass bulb. Periodic repurifications were carried out to guard against possible contamination during storage over long periods of time. Pressure measurements before and after freezing out in liquid nitrogen showed a noncondensable impurity content of less than 1 p.p.m.

The catalysts were prepared from "Baker Analysed" nickel oxide. The pure nickel oxide catalysts were made by mixing a portion of the nickel oxide with distilled water, drying, and heating to 1000° C. The cake of nickel oxide was then ground in an agate mortar until it would all pass a 30-mesh screen. This powder was then pressed into a flat disk at a pressure of 700 kg./cm.^{2}, which was then sintered at 1000° C. for 3 hours. In the case of catalysts containing lithia the water was replaced by a measured amount of lithium hydroxide solution and during drying the mixture was stirred at frequent intervals to prevent concentration of the lithium at the drying surface. The rest of the

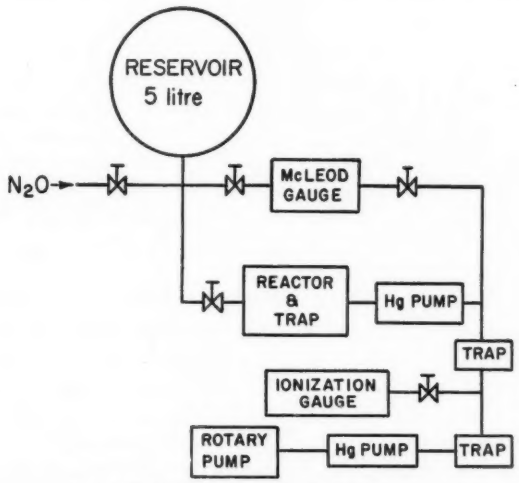

FIG. 1. Schematic diagram of the apparatus.

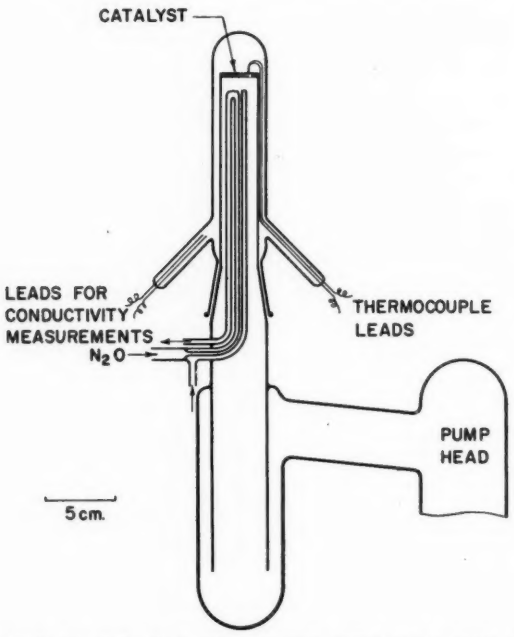

FIG. 2. Reactor. (The leads for conductivity measurements extend to the upper surface of the catalyst—this is not shown in the figure to avoid cluttering. No cooling of the capillary jacket—as indicated by the arrows—was employed in the present work, for reasons given in the text.)

preparative procedure was the same. Chromia was introduced by using a solution of ammonium dichromate.

Platinum wires were embedded in some of the catalysts before sintering to allow measurements to be made of the electrical conductivity under the reaction conditions.

RESULTS

Runs were made by filling the reservoir to a known pressure between 10^{-2} and 10^{-1} mm. with N_2O and allowing this to stream through the reactor. The pressure over the catalyst was proportional to the reservoir pressure and in a steady-state flow system the pressure of products can be taken as a measure of the rate of reaction at any instant. The reading of the ionization gauge was followed as the reservoir pressure dropped and was a measure of the variation of the rate with reactor pressure. Thus the kinetics of the reaction were easily studied even though no runs were carried out in which more than 1% decomposition occurred.

In the later runs the output of the ionization gauge was connected to a recording potentiometer. This increased the accuracy of the measurements, as it was possible to smooth the trace to reduce the effect of random fluctuations of the gauge reading.

In all experiments the apparatus was pumped down so that a reading of the order of 2×10^{-6} mm. was obtained on the ionization gauge with the catalyst at 500° C. This usually required about 16 hours when a new catalyst was used.

A typical run is shown in Fig. 3. The intercept on the axis at zero reservoir pressure represents the background pressure in the apparatus. It is clear that the reaction is first order with respect to the nitrous oxide. This first-order reaction was observed under

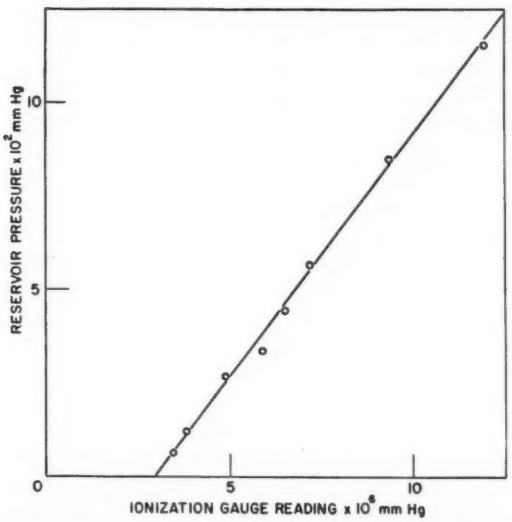

FIG. 3. Change of ionization gauge reading with reservoir pressure in a typical run (pure NiO catalyst), 442° C.

most experimental conditions. All the catalysts showed this behavior at temperatures above 400° C., but below this temperature pure NiO and NiO catalysts with up to 0.5 mole per cent lithia added showed a more complex behavior with an apparent order of reaction between 1.0 and 1.1. In cases where this complex order was observed the extrapolated rate for zero N_2O pressure was taken. This rate was found to fit well with the results taken at higher temperatures when the Arrhenius activation energy was determined.

All the results are reported in terms of the concentration of foreign ions added initially, since this appears to be the usual method of reporting such data and in terms of the surface concentrations is probably as meaningful as the analysis figures. Analysis showed, however, that about half of the added lithia distilled out of the samples during sintering.

Electrical-conductivity measurements were made on some of the catalysts during the course of the reaction using an a-c. bridge at 500 c./s. Additions of lithia had a marked effect on conductivity. One mole per cent of lithia, for example, increased the conductivity of the NiO by a factor of 10^4 at 400° C. and the apparent activation energy for conduction was lowered from 18.5 kcal. to 4.1 kcal. No attempt was made to measure the small conductivities of NiO with chromia added. There was a measurable increase in conductivity of pure NiO on admission of N_2O but this was small and tended to increase with time so that it could not be studied systematically.

The effects of the additions of foreign ions to the nickel oxide on the apparent activation energies for conduction and for the reaction are compared in Fig. 4. In the case of lithia additions the activation energy was lowered by 2 to $2\frac{1}{2}$ kcal. and the activity at 400° C. was reduced to about half that for pure NiO. Comparisons of activity are, however, of necessity very approximate since the variation is of the same order as the reproducibility of activity between different samples of catalysts of the same composition.

Additions of chromia increased the activation energy for the reaction to such an extent that a great loss of activity occurred in the temperature range used.

An attempt was made to obtain more information regarding the complex-order reaction

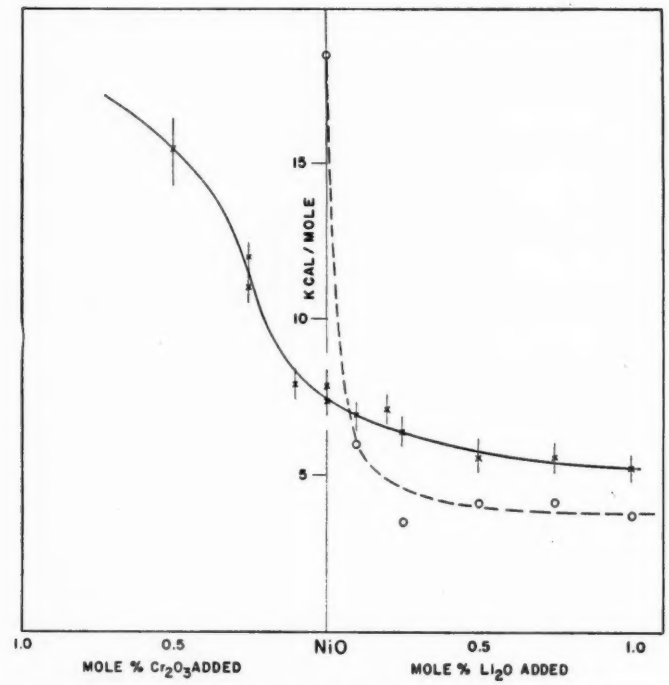

FIG. 4. Dependence of the observed activation energies for N_2O decomposition and electrical conductivity on catalyst composition. Solid line represents the activation energies for the N_2O decomposition (vertical lines indicate the probable experimental uncertainty). Broken line represents the activation energies for electrical conductivity.

occurring at lower temperatures. The results were not very reproducible but they suggested that a time-dependent loss of activity of the catalyst might be responsible for the deviation from a first-order reaction. The curvature of the plots of reaction rate against N_2O pressure was more marked after the catalyst had been evacuated at a high temperature just prior to the run. If two low-temperature runs were done consecutively, without raising the temperature in between, the first run showed a higher apparent order than the second.

DISCUSSION

Heterogeneous decomposition of nitrous oxide on a *p*-type semiconducting oxide catalyst and in the temperature region of interest in the present investigation may in general be considered in terms of the following reactions:

$$N_2O_{(g)} + S \rightleftharpoons N_2O_{(s)} \quad [1]$$

$$N_2O_{(s)} \rightarrow N_{2(g)} + O^-_{(s)} + \oplus \quad [2]$$

$$O^-_{(s)} + O^-_{(s)} + 2\oplus \rightleftharpoons O_{2(g)} \quad [3]$$

$$O^-_{(s)} + N_2O_{(g)} + \oplus \rightarrow N_{2(g)} + O_{2(g)} \quad [4]$$

$$O^-_{(s)} \rightleftharpoons O^-_{(s)} + \oplus \quad [5]$$

where S represents an adsorption site on the catalyst surface, $\oplus$ a "positive hole", and subscripts (g) and (s) indicate gas phase and chemisorbed particles, respectively. All

these reactions have been considered by different authors before. The experimental conditions were, in some instances, widely different, and varying emphasis was placed on the relative importance of the individual steps in the reaction scheme.

Amphlett (8) used a great excess of oxygen, containing only 10–1000 p.p.m. of N_2O. At a constant oxygen pressure the rate expression reduces under these conditions to

$$-d(N_2O)/dt = K(N_2O)$$

and is in agreement with the observed first order in N_2O. Under conditions employed in these experiments it is likely that reaction [4] is responsible for the decomposition of N_2O. The effect of controlled impurities was not investigated. The over-all activation energy was found to be dependent on the temperature range in which the measurements were made.

Hauffe, Glang, and Engell (6) have studied the decomposition of N_2O in the presence of comparable amounts of oxygen on nickel oxide and doped nickel oxide catalysts. Percentage conversions were measured as a function of temperature and the apparent order of the reaction and the activation energy were deduced by assuming constant values of these quantities throughout the temperature ranges covered. There was a marked dependence of both the order of the reaction and the activation energy on catalyst composition. It would be difficult to explain by a detailed mechanism the wide variation of the apparent order of the reaction, although it is possible that the apparent complexity may be due to the particular method employed in evaluating this quantity. There was, however, a distinct effect of the doping on the percentage conversion, and this was interpreted by Hauffe (10) in terms of an increase in the rates of reactions [3] and [4] with increasing concentration of positive holes. These two reactions are assumed to be slow and, therefore, the rate-determining ones under most conditions.

Under most of the experimental conditions in the present work a reaction rate of first order in nitrous oxide was observed. The decomposition of N_2O amounted to less than 1%. From the observed pressure in the ionization gauge and in view of the ratio of pumping speed of the mercury diffusion pumps it is estimated that the steady-state partial pressure of gaseous oxygen over the catalyst was of the order of 10^{-6} mm. or smaller. It is, therefore, likely that under these conditions interference by secondary chemisorption of oxygen, the reverse of reaction [3], was negligibly small. Inasmuch as this assumption is correct, primary chemisorption and splitting of N_2O must play the main role in the decomposition, and the measured rates and the observed activation energies are those of the chemisorption reactions [1] and [2] and not of the desorption reactions [3] and [4]. Reactions [1] and [2] cannot be expected to be affected directly by the concentration of positive holes in the catalyst unless $N_2O_{(s)}$ is a negative ion, in which case an increase in positive-hole concentration would only tend to accelerate the reverse of reaction [1]. The dependence on doping observed in the present work is, therefore, not explainable by a direct effect of positive-hole concentration on the rates of these reactions. The indirect effect of the concentration of positive holes on the surface coverage and therefore also on the heat of adsorption, on the other hand, appears to provide a satisfactory explanation of the doping effect.

An increase in the concentration of positive holes will speed up the desorption reactions, which are dependent on electron transfer to the catalyst, and decrease the surface coverage under the steady-state reaction conditions. In our experiments the surface coverages were very small and their variations due to doping could not have significant effect on the number of available surface sites. On the other hand, these variations should affect strongly the heats of adsorption. The heat of adsorption of oxygen on NiO has

been shown to be very strongly dependent on surface coverage. Dell and Stone (11) have made calorimetric measurements of the heat of adsorption on NiO films on the surface of metallic nickel and have found values falling from 54 kcal./mole for a surface largely depleted of oxygen to 20 kcal./mole for a surface with 10% of the B.E.T. surface area covered with oxygen. The theoretical work of Takaishi (12) suggests, subject to certain assumptions, that in the case of *p*-type semiconducting oxides the decline in the heat of adsorption with increasing surface coverage should be particularly large at very low coverages. Therefore, any increase in the rate of the desorption reactions (as, for example, due to doping with Li_2O) which results in a decrease in the steady-state concentration of chemisorbed oxygen will lead to an increase in its binding energy. It is reasonable to suppose that this will result in a reduction of the potential energy of the activated complex leading to the adsorbed oxygen and thus in a lowering of the activation energy for the reaction. These views are in agreement with the observed results. Doping with Li_2O to increase the concentration of positive holes results in a decrease in the observed activation energy in the predicted manner, while additions of Cr_2O_3 have the expected opposite effect. Furthermore, the activation energies observed in the present work are much lower than have been observed by other workers. In agreement with the expressed views this provides indirect evidence for very low surface coverages under the experimental conditions employed.

The apparent complex order observed at lower temperatures is qualitatively explainable by assuming some occurrence of reaction [5] under certain conditions. Gray and Darby (13) have made a thorough study of the different processes involved in the chemisorption of oxygen on nickel oxide. They find that the rate of desorption of oxygen is extremely slow at temperatures below about 300° and requires an apparent activation energy of the order of 60 kcal./mole. At lower reaction temperatures the reverse of [5] can therefore be relatively slow and thus lead to a build-up of surface oxygen which is removed slowly on evacuation. At higher reaction temperatures deviations from the first order were not observed. Also, with NiO doped with more than about 0.5 mole per cent of Li_2O no deviations from the first order were apparent. This is in agreement with the suggested explanation since doping with Li_2O would be expected to increase the rate of the reverse reaction [5].

The trend in activation energies of conductivity shown in Fig. 4 appears to be roughly comparable with the one established by Verwey *et al.* (14). The values of the activation energies are considerably lower than those of Keier, Roginski, and Sasonov (15) at comparable atomic concentrations of lithium. The somewhat different method of catalyst preparation and the different ambient atmosphere in the present work are probably responsible for the discrepancy. At the present state of knowledge of the physical and chemical phenomena involved it would be difficult to attempt a quantitative correlation between the observed activation energies for electrical conductivity and for the decomposition reaction in terms of the mechanism proposed for the latter.

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THE NON-ENZYMATIC HYDROLYSIS OF *p*-NITROPHENYL PHOSPHATE[1]

K. A. HOLBROOK[2] AND LUDOVIC OUELLET

ABSTRACT

The kinetics of the non-enzymatic hydrolysis of *p*-nitrophenyl phosphate have been studied in aqueous solution in the pH range 2.6 to 9.0 and at temperatures from 68.0° to 82.0° C. The reaction has been followed by colorimetric measurement of the nitrophenol produced by the reaction

$$O_2NC_6H_4OPO_3H^- + H_2O \rightarrow O_2NC_6H_4OH + H_2PO_4^-.$$

The reaction is first order with respect to *p*-nitrophenyl phosphate and has an activation energy of 26.0 kcal./mole at pH 2.6. An explanation has been proposed in terms of the different rates of hydrolysis of the various ionic species of the ester present in solution.

INTRODUCTION

Studies have been made of enzymatic hydrolyses of *p*-nitrophenyl phosphate by Morton (1) using alkaline phosphatases of cow's milk and calf intestinal mucosa and by Axelrod (2) using enzymes present in citrus juices. In both cases the hydrolysis produces inorganic phosphate and *p*-nitrophenol by the simple reaction

$$O_2NC_6H_4OPO_3H^- + H_2O \rightarrow O_2NC_6H_4OH + H_2PO_4^-.$$

In view of current theories (3, 4) of organic phosphate hydrolyses it seemed desirable to make a more complete study of this reaction over a wide range of pH in the absence of enzymes.

EXPERIMENTAL

Materials

p-Nitrophenyl phosphate (disodium salt) was supplied by Mann Research Laboratories Inc. and was used without further purification. A stock solution (about 8×10^{-2} *M*) was kept in cold storage. Analysis indicated the presence of about 0.5% *p*-nitrophenol in the original phosphate.

p-Nitrophenol used for calibration purposes was purified by boiling with dilute hydrochloric acid and activated charcoal. The recrystallized material had a melting point of 114.0° C.

Buffer solutions.—The following buffer solutions were used and their pH values at 76.9° C. (given in parentheses) were measured using Beckman high-temperature electrodes: acid potassium phthalate/hydrochloric acid (2.6), acid potassium phthalate (3.8), acetic acid/sodium acetate (4.7), acid potassium phthalate/potassium hydroxide (5.8), trishydroxymethylaminomethane/hydrochloric acid (7.4), boric acid/sodium hydroxide (9.0). The concentrations of these buffers were adjusted and potassium chloride was added to make the ionic strength of the reaction mixtures 0.1.

Procedure

Kinetic runs were done using the apparatus described in a previous paper (5). The rate of reaction was measured by following colorimetrically the concentration of *p*-nitrophenol produced, the method being similar to that of Axelrod (2). One-milliliter aliquots were extracted from the reaction mixture at convenient time intervals and diluted by adding to 10 ml. *M*/6 sodium hydroxide at room temperature. This effectively stops all

[1]*Manuscript received December 16, 1957.*
Contribution from the Department of Chemistry, University of Ottawa, Ottawa, Canada.
[2]*National Research Council Postdoctorate Fellow 1956–57.*

reaction (see Fig. 2) and produces the yellow color characteristic of the *p*-nitrophenylate ion. The absorbance of the solution was measured in a Beckman model DU spectrophotometer at 400 mμ at which wavelength there is strong absorption due to the salt form (6). The addition of 1 ml. of reaction mixture did not alter the pH of the sodium hydroxide sufficiently to affect the calibration. A standard calibration graph of absorbance versus *p*-nitrophenol concentration was prepared using the purified *p*-nitrophenol described above.

RESULTS

Order of the Reaction

The reaction at 76.9° C. was found to be first order with respect to *p*-nitrophenyl

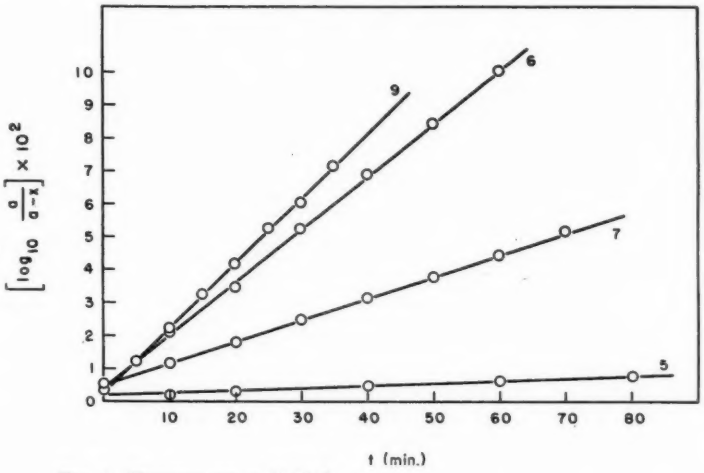

FIG. 1. Temperature = 76.9° C.

Run	5	7	6	9
Initial concn. phosphate $\times 10^3$ *M*	0.834	0.834	0.834	1.657
pH	7.4	5.8	4.7	2.7

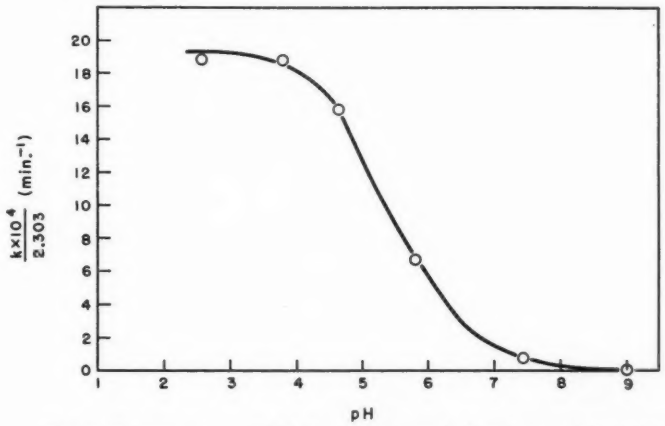

FIG. 2. Temperature = 76.9° C. *p*-Nitrophenyl phosphate = 0.834×10^{-3} *M*.

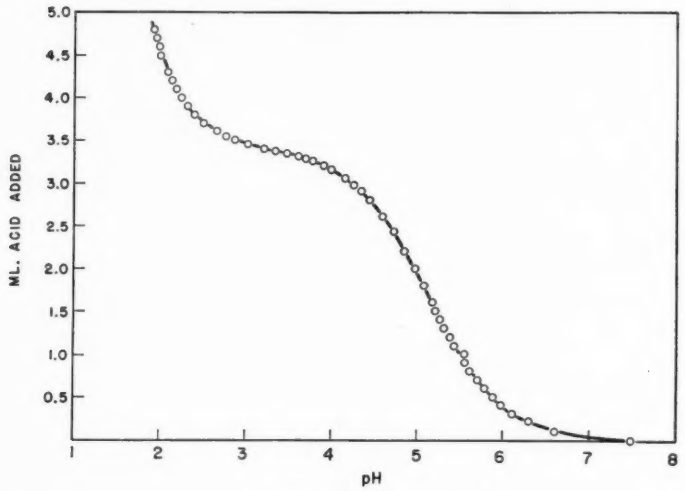

FIG. 3. Temperature = 25° C.

phosphate and first order with respect to time, over the first 10–20% hydrolysis. This is illustrated by plots of the first-order log function against time for different initial conditions of pH and phosphate concentration shown in Fig. 1.

The Effect of pH

Runs were done at different pH values from 2.6 to 9.0 at 76.9° C. and Fig. 2 shows a plot of the first-order rate constant against pH. For comparison, Fig. 3 shows a microtitration curve of *p*-nitrophenyl phosphate obtained (at 25° C.) using the standard procedure. It can be seen that the increase in rate obtained at lower pH values parallels the change in ionic form of the phosphate ester.

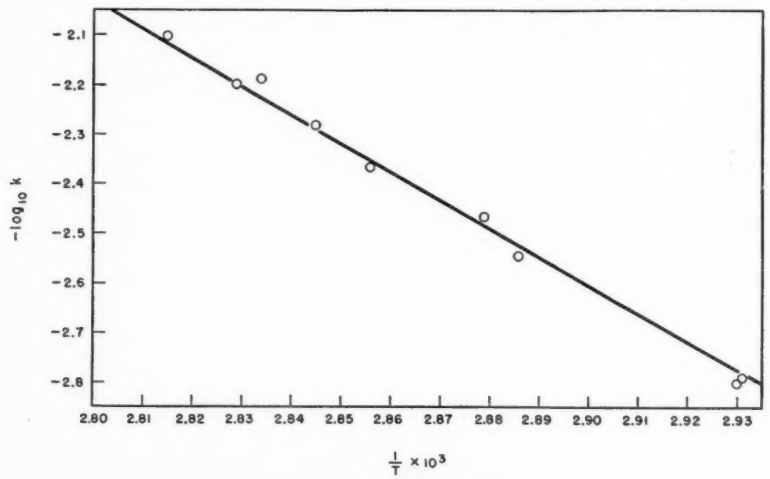

FIG. 4. pH = 2.6.

The Activation Energy

The activation energy corresponding to the first-order rate constant at pH 2.6 was obtained by measuring the rate as a function of temperature from 68.0° to 82.0° C. Fig. 4 shows a plot of $\log_{10}k$ versus $1/T°$ K.

DISCUSSION

Although the enzymatic hydrolyses of a number of organic phosphates have been studied at physiologically important pH values, relatively few attempts have been made to study these hydrolyses over a wide range of pH values in the absence of enzyme.

We have previously studied the non-enzymatic hydrolyses of ATP (7) and ADP (5) and have found that the effect of pH upon these hydrolyses could be explained in terms of the differing rates of hydrolysis of different ionic species present in solution.

The hydrolysis of *p*-nitrophenyl phosphate, which follows the simple over-all equation

$$NO_2.C_6H_4OPO_3H^- + H_2O \rightarrow NO_2.C_6H_4OH + H_2PO_4^-, \quad [1]$$

shows a similar relationship between the effect of pH (Fig. 2) and the titration curve of the ester (Fig. 3).

The inflection point in the latter at about pH 5.0 presumably corresponds to the equilibrium

$$NO_2C_6H_4OPO_3^= + H^+ \rightleftarrows NO_2C_6H_4OPO_3H^-.$$

At pH 9.0 it has been observed that the rate of hydrolysis is practically zero, when the ester is largely present as the completely ionized form $NO_2C_6H_4OPO_3^=$, whereas at pH 2.6–2.7, when the predominant ionic species present is the singly charged $NO_2C_6H_4OPO_3H^-$ (assuming no large variation in the equilibrium constant from 25° to 70° C.), the rate of hydrolysis is appreciable.

The general expression for the rate of hydrolysis between pH 2.6 and 9.0 can be written

$$\text{rate} = [H_2O]\{k_1[NO_2C_6H_4OPO_3H^-] + k_2[NO_2C_6H_4OPO_3^=]\},$$

where [*p*-nitrophenyl phosphate]$_0$ = $[NO_2C_6H_4OPO_3H^-] + [NO_2C_6H_4OPO_3^=]$. Hence under the conditions at pH 2.6, an approximation is

$$\text{rate} = k_1[H_2O]\,[p\text{-nitrophenyl phosphate}]_0.$$

At this pH, the first order of the reaction with respect to the phosphate ester has been demonstrated (Fig. 1) and the activation energy has been found to be 26.0 kcal. An entropy of activation $\Delta S_1 = -14.0$ e.u. (taking $[H_2O] = 55.5$ moles/liter) was calculated.

Whether the rate-determining hydrolysis of the singly charged species occurs by a C—O or O—P bond splitting is uncertain and could only be decided by H_2O^{18} experiments. The mechanism by which this step occurs may well involve a proton transfer as suggested by Westheimer and Kumamoto (8) for the hydrolysis of the mono anions of mono- and di-benzyl phosphates.

The entropy of activation of −14.0 e.u. is more negative than those found for the O—P splitting of the adenosine phosphates at alkaline pH values (5) although larger negative values have been reported by Friess (9) for ATP, pyrophosphoric acid, and triphosphoric acid under mildly acidic conditions. In a recent study of the hydrolyses of substituted phenyl phosphates, Chanley and Feageson (10) have noted that singly charged species tend to hydrolyze more rapidly than either the completely ionized or the uncharged species. This was explained in terms of Koshland's nucleophilic displacement mechanism (4) for such reactions.

Table I gives a comparison of the rates of hydrolysis of substituted aromatic phosphates observed by Chanley and Feageson (10) with our observed rate of hydrolysis of *p*-nitrophenyl phosphate under identical conditions. The rates are shown to increase in accordance with the increase in electrophilic character of the group attached to the phosphorus atom, as would be predicted from a nucleophilic displacement mechanism.

TABLE I

RATES OF HYDROLYSIS OF SOME AROMATIC PHOSPHATES

Compound	Dissociation constants		pH of reaction	Rate, $hr.^{-1} \times 10$, at 80° C.
	pk_1	pk_2		
Phenyl phosphate	1.00	5.88	3.83	1.16
m-Carboxyphenyl phosphate	0.85	3.91	2.36	1.61
p-Carboxyphenyl phosphate	0.88	4.20	2.31	3.07
p-Nitrophenyl phosphate	<2	~5	2.70	3.62

RÉSUMÉ

La cinétique de l'hydrolyse non-enzymatique du *p*-nitrophényl phosphate en solution aqueuse a été étudiée à des pH allant de 2.6 à 9.0 et à des températures allant de 68.0° C. à 82.0° C. La réaction a été suivie par la mesure colorimétrique du *p*-nitrophénol libéré selon la réaction

$$O_2NC_6H_4OPO_3H^- + H_2O \rightarrow O_2NC_6H_4OH + H_2PO_4^-.$$

La réaction est du premier ordre par rapport au *p*-nitrophényl phosphate et elle a une énergie d'activation de 26.0 kcal./mole à pH 2.6. On propose une explication en termes du taux d'hydrolyse des différentes espèces ioniques en solution.

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PHOTOLYSIS OF *n*- AND *i*-PROPYL PROPIONATE[1]

M. H. J. WIJNEN

ABSTRACT

The photolysis of *n*- and *i*-propyl propionate has been studied in the temperature range of 30° to 170° C. The results strongly indicate that the following three primary processes may occur:

$$C_2H_5COOC_3H_7 + h\nu \rightarrow C_2H_5CO + C_3H_7O, \quad [1a]$$

$$C_2H_5COOC_3H_7 + h\nu \rightarrow C_2H_5 + CO_2 + C_3H_7, \quad [1b]$$

$$C_2H_5COOC_3H_7 + h\nu \rightarrow C_2H_5COOH + C_3H_6. \quad [1c]$$

Based on these primary steps a qualitative explanation may be given for the formation of all reaction products.

INTRODUCTION

In previous investigations of methyl acetate (1), methyl d_3-acetate (2), and ethyl propionate (3) it could be shown that the main primary step in the photolysis of these esters consisted in the break of the ester into RCO and RO radicals. It was possible to obtain information on the reactivity and thermal stability of the RO radicals thus produced.

It seemed interesting to extend these investigations to higher-boiling esters. The photolysis of *n*- and *i*-propyl propionate has therefore been studied.

EXPERIMENTAL

The experimental technique is essentially the same as described elsewhere (1). A Hanovia S-500 medium pressure arc was used as the light source. The light of the S-500 arc was not filtered, and its intensity was varied by inserting wire gauze screens between reaction cell and arc. The amount of decomposition did not exceed 5% of the compound under investigation.

As reaction products of the photolysis of *n*-propyl propionate were observed: CO, CO_2, CH_2O, C_2H_4, C_2H_6, C_3H_6, C_3H_8, *n*-C_4H_{10}, *n*-C_5H_{12}, *n*-C_3H_7OH, and CH_3CH_2CHO. *n*-Propyl alcohol was determined by mass spectrometer analysis of the residue after all other products had been removed by Toepler pump at −120° C. The total volume of these products was measured, after which analysis was carried out by mass spectrometer.

The following reaction products were observed in the photolysis of *i*-propyl propionate: CO, CO_2, CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, *n*-C_4H_{10}, *i*-C_4H_{10}, *i*-C_5H_{12}, $\{CH(CH_3)_2\}_2$, CH_3CHO, CH_3COCH_3, $C_2H_5COCH_3$, $C_2H_5COC_2H_5$, and *i*-C_3H_7OH. The C_1 to C_5 hydrocarbons and the carbon oxides were pumped over at −130° C., measured, and analyzed by mass spectrometer. The other products such as ketones, isopropyl alcohol, and 2,3-dimethylbutane were determined by mass spectrometer analysis of the residue.

Typical results obtained at various temperatures by photolysis of *n*-propyl propionate are given in Table I, those obtained by photolysis of *i*-propyl propionate in Table II.

[1]*Manuscript received January 8, 1958.*
Contribution from the Chemical Division, Research and Development Laboratories, Celanese Corporation of America, Clarkwood, Texas.

TABLE I

PHOTOLYSIS OF *n*-PROPYL PROPIONATE AT VARIOUS TEMPERATURES

	Run number:					
	1	2	3	4	5	6
n-$PrPr_0 \times 10^{-17}$ molec./sec.	9.14	8.92	8.85	8.84	8.74	9.60
Temperature, ° C.	41	41	131	131	170	170
Intensity (relative, %)	100	9	100	9	100	9
	Rate of formation of products in molec./sec. cc. $\times 10^{-12}$					
n-Propyl alcohol	2.06	0.20	—	—	—	—
Propionaldehyde	0.10	—	—	—	—	—
n-Pentane	0.64	0.04	0.67	0.04	0.60	0.02
n-Butane	6.22	0.42	8.04	0.41	7.42	0.23
Propane	1.31	0.05	1.39	0.06	0.55	0.07
Propylene	3.93	0.25	3.26	0.23	3.50	0.20
Ethane	2.68	0.29	4.69	0.48	4.50	0.39
Ethylene	0.80	0.07	0.88	0.06	1.68	0.12
Formaldehyde	2.76	0.08	1.65	0.34	5.54	0.32
Carbon monoxide	10.48	0.74	11.08	0.91	14.08	0.90
Carbon dioxide	2.60	0.20	2.60	0.22	3.50	0.21
CO/CO_2	4.0	3.7	4.2	4.1	4.0	4.3
R_{C_3}/R_{CO_2}	2.3	1.7	2.0	1.5	1.3	1.4

TABLE II

PHOTOLYSIS OF *i*-PROPYL PROPIONATE AT VARIOUS TEMPERATURES

	Run number:					
	7	8	9	10	11	12
i-$PrPr_0 \times 10^{-17}$ molec./sec.	7.74	7.14	6.67	6.85	5.31	5.31
Temperature, ° C.	33	33	109	109	176	176
Intensity (relative, %)	100	9	100	9	100	9
	Rate of formation of products in molec./sec. cc. $\times 10^{-12}$					
i-Propyl alcohol	6.65	0.27	0.44	0.03	0.21	0.02
Acetaldehyde	7.58	0.29	10.66	0.69	7.12	0.55
Methyl ethyl ketone	1.04	0.06	—	—	—	—
Diethyl ketone	0.34	0.03	—	—	—	—
Methyl isopropyl ether	0.39	—	—	—	—	—
i-Pentane	2.23	0.13	2.63	0.19	2.18	0.15
2,3-Dimethylbutane	0.60	—	0.41	0.05	0.96	—
n-Butane	2.25	0.17	2.72	0.17	2.04	0.11
i-Butane	0.28	0.03	0.82	0.06	0.70	0.02
Propane	3.14	0.22	4.14	0.32	4.15	0.22
Propylene	5.66	0.41	6.32	0.43	5.75	0.42
Ethane	1.40	0.10	2.54	0.23	3.32	0.37
Ethylene	0.65	0.05	0.75	0.06	0.81	0.04
Methane	0.27	0.02	1.21	0.22	3.22	0.51
Carbon monoxide	9.56	0.70	10.20	0.98	10.28	0.82
Carbon dioxide	4.12	0.29	4.34	0.35	4.42	0.34
CO/CO_2	2.2	2.4	2.4	2.8	2.3	2.4

DISCUSSION OF RESULTS

n-Propyl Propionate

To explain the formation of products in the photolysis of *n*-propyl propionate the following primary steps are suggested:

$$n\text{-}C_2H_5COOC_3H_7 + h\nu \rightarrow C_2H_5CO + n\text{-}C_3H_7O, \quad [1a]$$

$$\rightarrow C_2H_5 + CO_2 + n\text{-}C_3H_7, \quad [1b]$$

$$\rightarrow C_2H_5COOH + C_3H_6. \quad [1c]$$

Steps [1*a*] and [1*b*] have been shown to occur in the photolysis of methyl acetate and ethyl propionate. Step [1*a*] produces *n*-propoxy and propionyl radicals. Propionyl radicals are known (4) to be quite unstable and decompose readily into ethyl radicals and carbon monoxide. The possibility that at 40° C. some C_2H_5CO radicals survive long enough to form diethyl ketone and possibly propyl ethyl ketone as has been observed in the case of isopropyl propionate may, however, not be excluded. Carbon monoxide is observed at all temperatures as the main reaction product. The presence of *n*-propoxy radicals is confirmed by the formation of *n*-propyl alcohol and of propionaldehyde at 40° C. Step [1*b*] produces ethyl and propyl radicals in addition to carbon dioxide. Accepting that practically all C_2H_5CO radicals decompose into C_2H_5 and CO, it would be expected that at any given temperature the ratio CO/CO_2 would be constant. This is confirmed by the results, as shown in Table I, which indicate that step [1*a*] occurs about four times as frequently as step [1*b*]. The presence of propyl radicals during the photolysis of *n*-propyl propionate is confirmed by reaction products such as propane, propylene, and pentane. The formation of butane, ethane, and ethylene confirms the presence of ethyl radicals, suggested to be formed by step [1*b*] and by step [1*a*] via the C_2H_5CO radical.

If reactions [1*a*] and [1*b*] were the only primary steps, then it would be expected that $R_{CO_2} = R_{C_3}$, where R_{C_3} is the rate of production of all compounds containing *n*-propyl radicals so that $R_{C_3} = R_{C_5H_{12}} + R_{C_3H_8} + R_{C_3H_6}$. Table I shows $R_{C_3} \gg R_{CO_2}$. This indicates that more products, containing propyl radicals, are formed than can be accounted for by step [1*b*]. To explain this, step [1*c*] has been suggested. Propionic acid in trace amounts is not detected by mass spectrometer analysis, as could be shown by adding small amounts of propionic acid to the *n*-propyl propionate residue of the photolysis before analysis. Confirmation for step [1*c*] may, however, be found (1) in the rather large amounts of propylene produced, especially if compared to the amounts of propane formed, and (2) in the fact that chemical analysis indicated the presence of an acid among the reaction products.

This investigation was mainly undertaken to obtain information regarding the *n*-propoxy radical. However, neither propyl alcohol nor propionaldehyde could be detected at 130° C. and higher temperatures. This seems to indicate that the *n*-propoxy radical is not very stable thermally. Since no hydrogen was observed among the reaction products, the results indicate that the *n*-propoxy radical decomposes into ethyl radicals and formaldehyde according to the reaction

$$n\text{-}C_3H_7O \rightarrow C_2H_5 + CH_2O. \qquad [2]$$

This type of decomposition reaction for the alkoxy radical has been suggested previously by other authors (5, 6). It is important to point out that relatively large amounts of formaldehyde were produced. In the extreme case where all *n*-propoxy radicals would decompose according to reaction [2], it would be expected that $R_{CO} = R_{CH_2O}$. This has not been observed. Since formaldehyde polymerizes easily it is probable that part of the formaldehyde was left behind in the apparatus as polymer and thus was not available for analysis.

The fact that no ethers were formed even at 40° C., which could conceivably be produced by recombination between alkyl and propoxy radicals, indicates that the concentration of propoxy radicals must be small. This is also confirmed by the fact that propionaldehyde, possibly a product of disproportionation reactions involving the propoxy radical, has only been observed in trace amounts at low temperatures.

i-Propyl Propionate

Primary steps similar to those suggested in the photolysis of *n*-propyl propionate will produce ethyl, *i*-propoxy, *i*-propyl, and propionyl radicals in addition to carbon oxides and propionic acid.

The isopropoxy radical has been suggested (6) to decompose according to the following reactions:

$$(CH_3)_2CHO \rightarrow CH_3 + CH_3CHO \quad [3]$$

and

$$(CH_3)_2CHO \rightarrow CH_3COCH_3 + H. \quad [4]$$

Reaction [3] is confirmed by the fact that large amounts of acetaldehyde were observed among the reaction products. The presence of methyl radicals is shown by the formation of methane and isobutane. Since it is not possible to decide to what extent methyl radicals are involved in the production of ethane and propane, it is difficult to draw a comparison between the amounts of acetaldehyde and methyl radicals produced by reaction [3]. No reliable data were obtained for the production of acetone although it could be established that some acetone was produced, especially at low temperatures. Since no hydrogen was observed, it is unlikely that acetone was formed by reaction [4]. More probable is the formation of acetone via disproportionation reactions involving the isopropoxy radical. Accepting primary steps [1*a*], [1*b*], [1*c*], and reaction [3], all other reaction products may be explained by abstraction, recombination, and disproportionation reactions of the radicals thus produced.

The fact that methyl ethyl ketone and diethyl ketone are found at 33° C. indicates some stability for the C_2H_5CO radical. This is in agreement with previous results for the photolysis of diethyl ketone, where a quantum yield of 0.6 (7) was observed for the production of CO at 25° C. The ratio R_{CO}/R_{CO_2} indicates that step [1*a*] occurs about 2.4 times as frequently as step [1*b*]. Comparison with the similar ratio for *n*-propyl propionate indicates that step [1*a*] is relatively more important for normal propyl propionate than it is for isopropyl propionate.

The sharp decrease of isopropyl alcohol formation with increasing temperature seems to indicate that the isopropoxy radical is not very stable thermally. In all respects our results indicate that both *n*- and *i*-propoxy radicals react very similarly and decompose readily by breakage of the carbon–carbon bond rather than by splitting off of hydrogen atoms.

ACKNOWLEDGMENTS

The author wishes to thank Dr. H. D. Medley for his constant interest in the fundamental research program of this laboratory. Special thanks are due to Mr. R. W. Jarrett and Mr. R. M. Guedin for calculation and interpretation of the mass spectrometer data.

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INFLUENCE OF WATER CONCENTRATION ON THE HYDROLYSIS OF UNSTABILIZED CELLULOSE NITRATE IN ACETONE/WATER SOLUTION[1]

PAUL E. GAGNON, KARL F. KEIRSTEAD,[2] BRIAN T. NEWBOLD, AND J. THOMAS

ABSTRACT

The influence of water concentration upon the hydrolysis of the sulphate acid ester in unstabilized cotton and wood cellulose nitrates in acetone/water solution at 25°±0.1° C. has been determined. When the water content of these systems was increased, the rate of hydrolysis of the sulphate acid ester in cotton or wood cellulose nitrates decreased. This effect was greatest in the first hour of hydrolysis. The presence of more than about 2% water in the acetone/water solution prevented the completion of hydrolysis after 24 hours.

INTRODUCTION

The hydrolysis of the sulphate ester in unstabilized cellulose acetate sulphate in acetone is rapid compared to that of the acetate ester (1). Recently, it was found that hydrolysis of the sulphate acid ester, RSO_4H, in unstabilized cotton and wood cellulose nitrate in acetone was rapid compared to that of the nitrate ester (2).

The hydrolysis of the sulphate ester in cellulose acetate sulphate in acetone is greatly affected by temperature and is complete after 24 hours at 25° C. (1). There is much evidence that the rate of solvolysis of the sulphate ester in a cellulose-mixed ester depends to a great extent upon the liquid medium employed (3, 4). It was shown previously that hydrolysis of the sulphate acid ester in unstabilized cellulose nitrate proceeded rapidly in 99% acetone/water, but was stopped in 90% acetone/water solution (2).

The object of the present work was to determine the influence of water concentration upon the hydrolysis of the sulphate acid ester in unstabilized cotton and wood cellulose nitrates.

EXPERIMENTAL

Cellulose Nitrate

The unstabilized cotton and wood cellulose nitrates were prepared by the method previously mentioned (5).

Hydrolysis of Unstabilized Cellulose Nitrate

The cellulose nitrates were washed and dried. Moist samples of different weights (2–5 g. for cotton and 3–7 g. for wood) were dissolved in acetone (700 ml.) containing 0.63% water, and hydrolysis experiments were carried out at 25°±0.1° C., using the method recently given (2). The initial acidity of the cellulose nitrates before hydrolysis started was determined by titration in 90% acetone (2).

In other experiments, moist samples of equal weight (2 g. for cotton and 5 g. for wood) of cellulose nitrates were dissolved in different acetone/water solutions (700 ml.) containing 0.63 to 4.20% water.

RESULTS AND DISCUSSION

Effect of Water Content of Cellulose Nitrate upon Hydrolysis of the Sulphate Acid Ester

The rates of hydrolysis of the sulphate acid esters in unstabilized cotton and wood

[1]*Manuscript received December 20, 1957.*
Contribution from the Department of Chemistry, Laval University, Quebec, Que., with financial assistance from the Defence Research Board of Canada.
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cellulose nitrates could not be strictly compared because the samples, although having the same ester content, had different water contents.

In view of the above observation it was of interest to determine the effect of water content upon the rate of hydrolysis of the sulphate acid ester in unstabilized cellulose nitrates. Accordingly, many experiments were performed using moist cotton cellulose nitrate samples of variable water content. For example, in two experiments, the rates of hydrolysis of the sulphate acid esters in 11.4% N cellulose nitrates having different water contents, 0.16 and 0.28%, were compared.

It was seen that the release of sulphuric acid was most rapid in the case of the cellulose nitrate containing least water. For instance, in the first experiment, after 5 minutes, the per cent sulphuric acid released was 1.58 whereas for the same time, in the second experiment, it was only 1.25. The difference between the water contents of the two cellulose nitrates concerned was only 0.12%. The effect of the water content was greatest upon the initial hydrolysis, that taking place in the first 15 minutes. Later, the hydrolysis proceeded normally. For instance, in the above experiments, the percentages of sulphuric acid released after 30 minutes were about the same, 2.07 and 2.13 respectively. Similar results were obtained with unstabilized wood cellulose nitrates.

It is evident that small differences in the water content had a significant effect upon the rate of hydrolysis of the sulphate acid ester, RSO_4H, as shown in Fig. 1 for two cotton cellulose nitrates containing 100% sulphate acid ester and 11.4 and 9.7% nitrogen respectively.

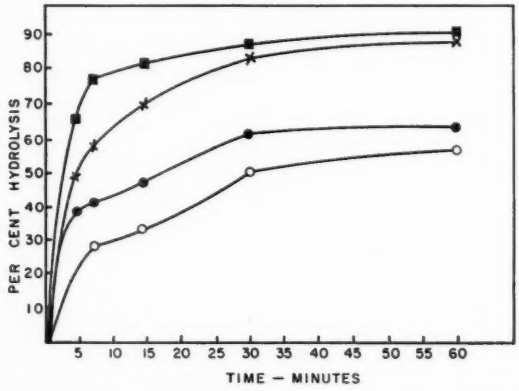

FIG. 1. Effect of water content of cellulose nitrate upon hydrolysis of sulphate acid ester.

	■	×	●	○
Nitrogen, %	11.4	11.4	9.7	9.7
Sulphate, % H_2SO_4, grav.	2.38	2.38	1.54	1.54
Water concn., % vol.	0.16	0.28	0.42	0.57

When the water content was increased, the rate of hydrolysis of the sulphate acid ester in unstabilized cotton cellulose nitrate decreased. Similar results were obtained with wood cellulose nitrate.

Effect of Water Content of Acetone upon Hydrolysis of Sulphate Acid Ester

The hydrolysis of the sulphate acid ester in both unstabilized cotton and wood cellulose nitrates was stopped in the presence of acetone containing 10% water (2).

In the present work, the effect of the water content of the acetone hydrolysis medium upon the rate of hydrolysis of the sulphate acid ester in unstabilized cellulose nitrates was carefully investigated. Hydrolysis experiments were carried out using cotton cellulose nitrate samples containing about the same amount of water, dissolved in various acetone/water solutions. For example, cellulose nitrates containing about 11.4% nitrogen, 100% sulphate acid ester, and 0.13% water, expressed as % vol. in the acetone medium, were used for hydrolysis experiments.

It was seen that the rate of hydrolysis decreased as the water content of the acetone increased. For instance, 0.54% sulphuric acid was released in the first 5 minutes of hydrolysis when the acetone contained 0.63% water, in one experiment, whereas in another none was released with 4.20% water present in the acetone. In some experiments, there was 100% hydrolysis of the sulphate acid ester, but in others the hydrolysis was not complete after 24 hours because of the presence of too much water in the acetone.

The effect of the water content of the acetone upon the rate of hydrolysis of the sulphate acid ester in an unstabilized cotton cellulose nitrate is shown in Fig. 2. It is seen that increase of water content greatly reduced the rate of hydrolysis in the first hour. For example, with only 0.63% water in the acetone medium there was about 78% hydrolysis after 1 hour, whereas with a water content of 4.20%, the corresponding value was only 6%.

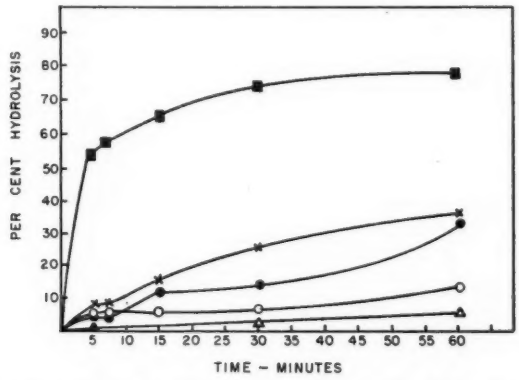

FIG. 2. Effect of water content of acetone upon hydrolysis of sulphate acid ester in cotton cellulose nitrates.

	■	×	●	○	△
Nitrogen, %	11.4	11.4	11.3	11.3	11.4
Sulphate, % H_2SO_4, grav.	0.94	0.81	0.85	0.79	0.81
Water concn., in acetone, % vol.	0.63	1.34	2.06	3.49	4.20
Sulphate acid ester, %	100	100	100	83	79

Furthermore, hydrolysis experiments were performed on unstabilized wood cellulose nitrates, and the results obtained for a sample containing about 10.7% nitrogen, 100% sulphate acid ester, and 0.35% water, expressed as % vol. in the acetone medium, were similar to those given by cotton cellulose nitrates.

The effect of the water content of the acetone medium upon the rate of hydrolysis of the sulphate acid ester in a wood cellulose nitrate is shown in Fig. 3. The results were very similar to those obtained with cotton cellulose nitrate (Fig. 2).

In the present work, cotton and wood cellulose nitrates containing 100% sulphate

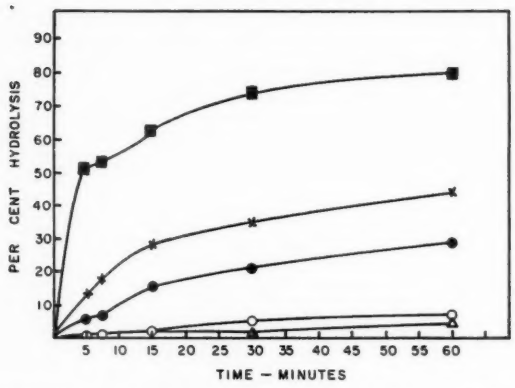

FIG. 3. Effect of water content of acetone upon hydrolysis of sulphate acid ester in wood cellulose nitrates.

	■	×	●	○	△
Nitrogen, %	10.8	10.7	10.6	10.6	10.7
Sulphate, % H_2SO_4, grav.	1.62	1.79	1.35	1.34	1.79
Water concn., in acetone, % vol.	0.63	1.34	2.06	3.49	4.20
Sulphate acid ester, %	100	99	91	67	62

acid ester were used. In some experiments, in the case of both cotton and wood cellulose nitrates, the sulphate acid ester content determined by the hydrolysis method (6) was too low in comparison to the true value, 100%. For instance, the ester contents for two cotton cellulose nitrates were 83 and 79%, and for wood cellulose nitrates, they were 67 and 62%, respectively. These low results were due to the fact that the sulphate acid ester was not completely hydrolyzed after 24 hours.

The effect of the increase in water content upon the degree of hydrolysis of the sulphate acid ester in both cotton and wood cellulose nitrates after 24 hours is shown in Fig. 4.

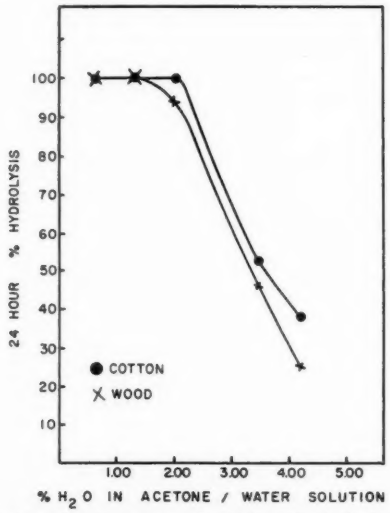

FIG. 4. Effect of water content of acetone upon the 24-hour hydrolysis of sulphate acid ester in cellulose nitrates.

It is evident that with less than 2% water in the acetone the sulphate acid ester is completely hydrolyzed after 24 hours; but with higher water contents, the degree of hydrolysis decreases rapidly.

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L'ARYLATION DES QUINONES PAR LES SELS DE DIAZONIUM

I. SUR LA SYNTHÈSE DES MONOARYL-*p*-BENZOQUINONES[1]

P. BRASSARD[2] ET P. L'ÉCUYER

RÉSUMÉ

Une étude de la réaction des sels de diazonium avec la *p*-benzoquinone a été faite. Exécutée selon des conditions bien déterminées quant à la nature du solvant, la concentration de la solution tampon et la température du milieu, cette réaction constitue une excellente méthode générale de synthèse des monoaryl-*p*-benzoquinones.

INTRODUCTION

Borsche (1, 2) réussit, en 1899, la première synthèse d'une monoaryl-*p*-benzoquinone. Par l'action d'un grand excès de chlorure de benzène-diazonium sur le *p*-nitrosophénol en milieu alcalin, il parvint à isoler le 2-phényl-4-nitrosophénol et le 2,6-diphényl-4-nitrosophénol dont la réduction en aminophénols et l'oxydation de ces derniers ont fourni, avec un rendement insignifiant, les 2-phényl- et 2,6-diphényl-*p*-benzoquinones. La très sérieuse difficulté de cette préparation réside dans l'isolement et la purification du phénylnitrosophénol.

En 1924, Günther (3) rapporta la première préparation de quelques monoaryl-*p*-benzoquinones par l'action de sels de diazonium sur la *p*-benzoquinone en solution alcoolique diluée et en présence d'acétate de sodium. Enfin, en 1934, Kvalnes (4) modifia la méthode de Günther pour préparer quelques autres monoaryl-*p*-benzoquinones dont le résidu phényle est porteur d'un substituant en position 4. Il ne fait aucune mention du rendement des quinones pures.

Cette modification comporte à peu près les mêmes inconvénients que la méthode originale de Günther. En effet, l'une et l'autre ne sont réalisables qu'avec les sels de diazonium porteurs d'un substituant en position 4 ou en 3, à la condition dans ce dernier cas qu'il soit fortement électronégatif. Autrement la réaction ne marche pas, comme Kvalnes l'admet lui-même à la suite de son insuccès à préparer les *o*-nitrophényl-, 2,6-xylényl- et α-naphtyl-*p*-benzoquinones.

D'ailleurs, quelques-unes des préparations décrites par Kvalnes, lorsque reprises par Asano et Kameda (5), se sont avérées beaucoup moins efficaces tant au point de vue des rendements que de l'homogénéité du produit. Celui-ci est toujours contaminé par une certaine quantité de substances polysubstituées dont il est souvent difficile de se débarrasser.

Enfin, en 1950, Schimmelschmidt (6), en utilisant le bicarbonate de sodium en milieu aqueux, a synthétisé l'*o*-chloro-, l'*o*-nitro- et d'autres phénylquinones ayant dans le résidu aromatique plusieurs substituants dont un halogène en position 2.

Cette dernière modification constitue sous certains aspects une amélioration appréciable à la méthode de Günther. Cependant le bicarbonate de sodium donne une solution tampon alcaline dans les conditions suivies par Schimmelschmidt. Or une étude de l'influence du pH du mélange sur la réaction nous a permis de constater que le pH idéal est 5. Un pH plus élevé entraîne invariablement la formation de résines.

Il est vrai que Schimmelschmidt a obtenu un excellent rendement dans la préparation

[1]*Manuscrit reçu le 22 octobre 1957.*
Contribution du Département de Chimie, Faculté des Sciences, Université Laval, Québec, Qué. Ce mémoire est tiré de la thèse de doctorat de P. Brassard.
[2]*Adresse actuelle: Chemisches Institut der Universität, Zürich.*

de l'*o*-chlorophénylquinone, mais cela doit être attribué au fait que dans ce cas particulier la distillation du produit de la réaction donne un meilleur rendement que l'extraction et la cristallisation pour la purification de la quinone.

Les autres travaux portant sur la préparation de monoaryl-*p*-benzoquinones revêtent un caractère plutôt théorique. Wieland (7), en 1934, obtint la phényl-*p*-benzoquinone par la décomposition du phénylazotriphénylméthane en présence d'un excès de *p*-benzoquinone dans le benzène et aussi par l'interaction de l'acétate de benzène-diazonium et de la *p*-benzoquinone dans l'acide acétique anhydre.

Huisgen et Horeld (8), en 1949, ont pu mettre en évidence la réactivité de la *N*-nitrosoacétanilide à l'égard de la *p*-benzoquinone dans un solvant non-polaire tel que le benzène. La séparation des produits de la réaction par chromatographie leur a permis d'isoler la phényl-*p*-benzoquinone avec un rendement de 30%. Auparavant, Akagi et Hirose (9) avaient montré que le même réactif dans l'éthanol est encore plus efficace, mais donne également lieu à la formation de quantités appréciables de produits bisubstitués.

De ce qui précède il ressort que les méthodes employées à date pour la synthèse des monoaryl-*p*-benzoquinones laissent à désirer. C'est pourquoi il nous a paru opportun d'étudier la réaction des sels de diazonium avec la *p*-benzoquinone. Dans ce but, nous avons recherché l'influence qu'exercent sur le rendement et la pureté des produits normaux, les facteurs suivants: la nature et le volume du solvant, la nature et la concentration de la solution tampon, la température du milieu, la nature de l'anion du sel de diazonium et enfin la nature et la position du substituant.

Dans cette étude nous avons constaté que pour les sels de diazonium parasubstitués, la réaction, même à une température aussi basse que 15°, procède très rapidement et est peu influencée par de grandes variations des conditions d'opération. Nous avons alors concentré notre attention sur les autres sels de diazonium et voici les constatations que nous avons faites.

Il est à noter que pour cette étude de l'influence des diverses variables nous avons utilisé le sel de l'*o*-méthylbenzène-diazonium qui est un de ceux qui ne réagissent pas avec la *p*-benzoquinone dans les conditions suivies par Kvalnes.

Influence de la nature et du volume du solvant

La substitution d'un milieu aqueux à un solvant organique plus ou moins dilué améliore grandement le rendement et facilite la purification du produit obtenu. Une trop forte proportion de solvant organique rend impossible l'isolement de la moindre trace d'*o*-tolyl-*p*-benzoquinone. Même en faibles quantités, les solvants organiques favorisent diverses réactions secondaires et surtout la désamination.

Des sels de diazonium employés, seul ceux de deux amines, le *p*-aminophénol et l'acide *p*-aminobenzènesulfonique, donnent de meilleurs résultats dans l'alcool que dans l'eau. L'emploi de l'alcool à 65% dans la préparation de la *p*-hydroxyphényl-*p*-benzoquinone a probablement pour effet de réprimer la dissociation de la fonction phénolique et éviter l'humification. Dans le cas de l'acide sulfanilique, l'alcool est préférable à l'eau comme solvant, parce que la réaction s'accompagne de la salification de la fonction sulfonique et le sel est soluble dans l'eau, mais insoluble dans l'alcool.

Le volume du solvant a peu d'influence sur le cours de la réaction. On note, néanmois, une légère diminution des rendements en deçà et au delà d'un volume d'environ un litre pour $\frac{1}{10}$ de mole des réactifs. Quand la quantité d'eau employée est trop faible, une quantité variable de *p*-benzoquinone est enrobée par le produit de la réaction avant de pouvoir passer en solution. D'autre part, un trop grand volume de solvant augmente la formation de phénols (Tableau I).

TABLEAU I

INFLUENCE DU SOLVANT

Solvant organique, ml.	Eau, ml.	$NaOAc.3H_2O$ en moles	Rdt. d'*o*-tolylquinone	
			Produit brut, %	Produit pur, %
—	1000	0.225	78	58
Ethanol (200)	50	0.300	—	0
Ethanol (200)	800	0.300	64	41
Acétone (200)	800	0.300	—	—
Formamide (150)	100	0.300	—	0

Influence de la nature et de la concentration de la solution tampon

La nature et la concentration de la solution tampon, tout comme dans la réaction de Meerwein, s'avère d'une importance primordiale. De toutes les substances déjà utilisées par Meerwein (10), Schimmelschmidt (6) et surtout Rondestvedt et Vogl (11), c'est l'acétate de sodium qu'il est préférable d'employer dans la proportion de 2 moles par mole de réactif. Le pH du mélange réactionnel est alors 5.

En faisant varier la quantité d'acétate de sodium de 2 à 5 équivalents, la vitesse de la réaction s'accélère et le rendement du produit brut s'accroît, mais sa qualité se détériore graduellement avec l'augmentation de la concentration de l'acétate. Il s'ensuit en définitive une diminution du rendement de la substance pure; car il se forme une quantité proportionnelle de produits de décomposition et on éprouve une difficulté croissante à purifier la substance recherchée (Tableau II).

TABLEAU II

INFLUENCE DE LA CONCENTRATION D'ACÉTATE DE SODIUM HYDRATÉ

Température		Poids de $NaOAc.3H_2O$ en grammes	Rdt. d'*o*-tolylquinone	
Initiale	Finale		Produit brut, %	Produit pur, %
10°	25°	27.2 (0.200 m.)	77	65
10°	25°	30.6 (0.225 m.)	78	62
10°	25°	34.0 (0.250 m.)	83	53
10°	25°	40.8 (0.300 m.)	89	—
20°	30°	68.0 (0.500 m.)	95	30

Influence de la température

La température initiale optimum de la réaction se situe entre 10° et 15° pour tous les sels de diazonium. A cette température le dégagement gazeux se fait à une vitesse convenable et l'aryl-*p*-benzoquinone qui précipite est relativement pure. A moins de 10°, en l'absence d'un excès d'acétate, le produit formé prend généralement une teinte verdâtre indiquant la formation de quinhydrone. Par contre, il y a avantage à laisser le mélange se réchauffer lentement et atteindre la température ambiante vers la fin de la réaction, pour que se complète heureusement la transformation du composé intermédiaire. Une baisse de température à ce moment favorise la formation de sous-produits phénoliques, tandis qu'une température initiale supérieure à 15° ou une élévation trop rapide de celle-ci entraîne invariablement la formation de goudrons (Tableau III).

Influence de la nature de l'anion du sel de diazonium

Contrairement à ce qui se produit dans la réaction de Meerwein où seul l'emploi du chlorure et, dans une plus faible mesure, du bromure est possible, le chlorure, le bromure,

TABLEAU III

INFLUENCE DE LA TEMPÉRATURE

Température		$NaOAc.3H_2O$ en moles	Rdt. d'*o*-tolylquinone	
Initiale	Finale		Produit brut, %	Produit pur, %
4°	20°	0.225	78	60
10°	25°	0.225	78	62
15°	25°	0.225	78	58
20°	30°	0.250	71	43

le phosphate et le sulfate de diazonium réagissent indifféremment avec la *p*-benzoquinone (le sulfate requiert une plus grande quantité d'acétate pour neutraliser l'ion bisulfate) sans que le rendement ne soit affecté d'une façon appréciable. Seul le nitrate s'avère insatisfaisant, en donnant lieu à la formation de produits de décomposition (Tableau IV).

TABLEAU IV

INFLUENCE DE L'ANION DU SEL DE DIAZONIUM

Température		$NaOAc.3H_2O$ en moles	Acide en mole	Rdt. d'*o*-tolylquinone	
Initiale	Finale			Produit brut, %	Produit pur, %
10°	25°	0.225	HCl (0.3)	78	62
10°	25°	0.225	HBr (0.3)	77	60
10°	25°	0.425	H_2SO_4 (0.25)	78	61
10°	25°	0.225	H_3PO_4 (0.3)	76	—
10°	25°	0.225	HNO_3 (0.3)	71	—

Influence du chlorure cuivrique comme catalyseur

Ce catalyseur, employé dans la réaction de Meerwein, nuit à la réaction. Toutefois, en opérant dans l'acétone aqueux à 20% et à pH = 3, il a été possible d'isoler de l'*o*-chlorophényl-*p*-benzoquinone à peu près exempte de goudrons. Malgré tout, la substance était encore contaminée par une certaine quantité de produits huileux provenant sans doute d'une réaction secondaire du type de celle de Sandmeyer. D'ailleurs, l'addition fréquente de quantités appréciables du catalyseur devenait essentielle au maintien d'une vitesse convenable du dégagement gazeux.

Influence de la nature et de la position de substituant

Le rendement semble peu affecté par la nature du substituant dans le sel de diazonium. L'allusion maintes fois répétée (12, 13, 14, 15, 16) à l'effet que la présence d'un groupe méthoxyle diminue le rendement dans la réaction de Meerwein ne s'applique pas ici ni dans le travail de Rondestvedt et Vogl (17).

L'arylation par les sels de diazonium substitués en position 2 s'effectue avec d'excellents rendements à la condition que le substituant ne soit ni fortement électropositif ni trop électronégatif, mais il importe d'opérer dans des conditions nettement déterminées, car autrement les rendements peuvent diminuer considérablement et la pureté du produit se déteriorer à un point où il est difficile d'en isoler une substance pure.

Lorsque le substituant en 2 est très électronégatif ou très électropositif, on obtient malgré toutes les précautions une certaine proportion de polymères, d'hydrocarbures, de phénols et même de diazoiques résultant de la copulation du sel de diazonium avec les phénols.

La plupart des phényl-*p*-benzoquinones substituées en position 2 du résidu hydrocarbonné sont très solubles dans les solvants organiques et ont un point de fusion assez bas, de sorte que leur purification présente des inconvénients et des difficultés. Il est alors préférable d'extraire le produit brut à l'éther de pétrole bouillant, d'évaporer à sec l'extrait éthéré, de traiter le résidu au noir animal et ensuite de le cristalliser ou distiller sous vide. Toutefois, même en opérant dans les conditions les plus favorables, les rendements des monoaryl-*p*-benzoquinones obtenues à partir de sels de diazonium *o*-substituées sont inférieurs de 10% à 30% à ceux qui proviennent des isomères para.

Enfin, il semble que l'encombrement stérique en 2 joue un rôle très négligeable dans la réaction. Ainsi le sel de diazonium de l'*o*-aminodiphényle donne, malgré la grosseur du substituant, un rendement de 88% d'*o*-diphényl-*p*-benzoquinone pure. De plus, il est vrai que la 2,6-diméthylaniline ne donne qu'un faible rendement même du produit brut; mais, lorsque la réactivité de cette amine est rehaussée par la bromuration en 4, la réaction procède avec facilité pour fournir un excellent rendement de 2,6-diméthyl-4-bromophényl-*p*-benzoquinone.

Quelques-unes des synthèse décrites par Kvalnes ont été répétées en tenant compte des conditions les plus favorables telles qu'établies antérieurement. Dans tous les cas, les rendements de la substance brute approchaient 100% et, après purification, le pourcentage de récupération a toujours été supérieur à 90%. Plusieurs autres monoaryl-*p*-benzoquinones, même celles qu'il serait impossible d'obtenir par la méthode de Kvalnes, ont été synthétisées avec d'excellents rendements (Tableau V).

TABLEAU V

MONOARYL-*p*-BENZOQUINONES

Groupe substituant	Rdt., %	P.f., °C.	Formule	C		H	
				Calculé	Trouvé	Calculé	Trouvé
Phényle (10)	84	113–114					
p-Hydroxyphényle	59	176–178	$C_{12}H_8O_3$	72.00	71.8	4.03	4.3
p-Anisyle (10)	93	118–120					
p-Chlorophényle	88	129.5	$C_{12}H_7O_2Cl$	65.92	65.7	3.21	3.3
p-Nitrophényle (10)	89	136–137					
3,4-Diméthoxyphényle (1)	84	134–135					
m-Tolyle	81	86–87	$C_{13}H_{10}O_2$	78.77	78.6	5.09	5.1
m-Chlorophényle	90	142–143	$C_{12}H_7O_2Cl$	65.92	66.1	3.21	3.4
m-Acétophényl	84	96–97	$C_{14}H_{10}O_2$	74.33	74.3	4.46	4.6
o-Tolyle	62	59–60	$C_{13}H_{10}O_2$	78.77	78.5	5.09	5.1
o-Anisyle	81	58–59	$C_{13}H_{10}O_3$	72.88	72.5	4.71	4.7
o-Diphényle	88	168–170	$C_{18}H_{12}O_2$	83.06	82.8	4.65	4.7
o-Chlorophényle (16)	79	82–83					
o-Bromophényle	75	98–100	$C_{12}H_7O_2Br$	54.78	54.5	2.68	2.8
o-Carbométhoxyphényle	81	107–109	$C_{14}H_{10}O_4$	69.42	69.5	4.16	4.3
o-Nitrophényle (16)	76	99–101					
2,6-Diméthyl-4-bromophényle	83	82–84	$C_{14}H_{11}O_2Br$	57.75	57.7	3.81	3.9
2,6-Dichlorophényle (16)	73	104–106					
α-Naphtyle	78	76–78	$C_{16}H_{10}O_2$	82.04	81.9	4.30	4.5
Méthane sulfonate de 2-hydroxyphényle	77	148–148.5	$C_{13}H_{10}O_5S$	56.11	56.5	3.62	3.7

PARTIE EXPÉRIMENTALE*

La synthèse des monoaryl-*p*-benzoquinones décrites dans ce mémoire a été réalisée en tenant compte des conditions optimum d'opération telles qu'établies dans la partie théorique. Comme la façon de préparer les sels de diazonium et d'effectuer leur réaction avec la *p*-benzoquinone est à peu près constamment la même pour toutes les synthèses,

**Les points de fusion ont été pris à l'aide de l'appareil de Johns. Les combustions ont été faites par les auteurs.*

nous ne la donnons en détail que pour la première, nous contentant d'en mentionner, le cas échéant, les modalités.

Un excès de 20% de quinone facilite la purification du produit de la réaction. L'excès de quinone reste en solution dans les eaux-mères. Au contraire, l'emploi de quantités équivalentes de sels de diazonium et de quinone occasionne la formation de résines.

Phényl-p-benzoquinone (*10*)

Une solution d'aniline (9.3 g., 0.1 mole) dans 25 ml. d'acide chlorhydrique concentré étendu de 100 ml. d'eau est refroidie à une température inférieure à 5° et diazotée, en agitant régulièrement, par l'addition goutte à goutte d'une solution de 7.0 g. de nitrite de sodium dans 25 ml. d'eau. On vérifie la fin de la réaction à l'aide de papier iodo-amidonné. La solution ainsi obtenue est ensuite versée d'un seul trait dans une suspension de *p*-benzoquinone (13.0 g., 0.12 mole) dans 850 ml. d'eau à 15° qui contient en solution 30.6 g. (0.225 mole) d'acétate de sodium hydraté comme tampon. On agite énergiquement au moyen d'un agitateur mécanique.

Le dégagement gazeux qui caractérise la réaction commence immédiatement et le mélange se réchauffe lentement pour atteindre finalement la température ambiante. Après une heure d'agitation la réaction est terminée. On filtre la solution et on recueille 16.9 g. de produit brut sous forme d'une poudre jaune qu'on cristallise dans l'éther de pétrole (p.é. 65°–110°). Après avoir laissé séjourner la solution pendant quelque temps au réfrigérateur à −10°, on la filtre et on recueille 15.4 g. de phényl-*p*-benzoquinone pure cristallisée en paillettes jaune doré.

p-Hydroxyphényl-p-benzoquinone

On diazote comme précédemment 10.9 g. de *p*-aminophénol dissous dans 50 ml. d'eau et 14 g. d'acide sulfurique concentré et on verse cette solution dans un mélange de 13.0 g. de *p*-benzoquinone, de 54.4 g. d'acétate de sodium hydraté et 200 ml. d'alcool éthylique, tout en agitant mécaniquement. La réaction commence immédiatement à 15° et elle est terminée à la température ordinaire après 2 heures d'agitation. Après dilution avec un assez grand volume d'eau (environ 1 litre) la majeure partie du liquide surnageant le précipité est décantée et la *p*-hydroxyphényl-*p*-benzoquinone, qui s'est séparée sous forme de cristaux rouges, est filtrée. Elle cristallise dans l'alcool dilué en fines aiguilles rouges.

p-Anisyl-p-benzoquinone (*10*)

La réaction entre le chlorure de diazonium de la *p*-anisidine (12.3 g.) et la *p*-benzoquinone (13.0 g.) se fait en 30 minutes. On cristallise dans l'acétone aqueux (2:1) et on récupère 19.9 g. de *p*-anisyl-*p*-benzoquinone sous forme de lamelles rouges.

p-Chlorophényl-p-benzoquinone

On diazote de la façon habituelle, entre 5° et 10°, de la *p*-chloraniline (12.8 g.) et on fait réagir la solution du sel de diazonium avec la *p*-benzoquinone (13.0 g.) dans 1000 ml. d'eau à la température ambiante. La réaction dure 3 heures. On obtient 21.4 g. de produit pulvérulent jaune pâle. Après cristallisation dans un mélange d'alcool éthylique et d'acétone (2:1), on recueille 19.2 g. de *p*-chlorophényl-*p*-benzoquinone pure cristallisée en aiguilles jaunes.

p-Nitrophényl-p-benzoquinone (*10*)

La *p*-benzoquinone (13.0 g.) dans 1350 ml. d'eau à 20° réagit pendant 2 heures avec le sel de diazonium de la *p*-nitraniline (13.8 g.). La réaction terminée, on filtre le précipité jaune-orangé. On cristallise dans un mélange d'éthanol et d'acétone (2:1) pour obtenir 20.3 g. de *p*-nitrophényl-*p*-benzoquinone pure sous la forme d'aiguilles jaune-orangé.

3,4-Diméthoxyphényl-p-benzoquinone (*1*)

La réaction du chlorure de diazonium de la 3,4-diméthoxy-aniline (15.3 g.) avec la *p*-benzoquinone (13.0 g.) commencée à 12°, en présence de 34.0 g. d'acétate de sodium hydraté, se termine en moins d'une heure à la température ambiante. Après refroidissement du mélange on filtre le précipité rouge et on le cristallise dans un mélange éthanol–acétone (2:1). On obtient la 3,4-diméthoxy-*p*-benzoquinone pure (20.3 g.) sous la forme de lamelles rouges.

m-Tolyl-p-benzoquinone

On fait réagir le chlorure de diazonium de la *m*-toluidine (10.7 g.) avec la *p*-benzoquinone (13.0 g.). La réaction met plusieurs heures à se compléter. On obtient, par filtration, 18.4 g. de produit jaune brunâtre. On extrait celui-ci plusieurs fois à l'éther de pétrole (p.é. 65°–110°) bouillant. On évapore à sec sous pression réduite les extraits réunis, on dissout le résidu dans un mélange d'acétone, de méthanol et d'eau (1:1:1) et on bout cette solution pendant 15 minutes avec du noir animal. Après filtration à chaud et refroidissement à −10° pendant quelques jours, la *m*-tolyl-*p*-benzoquinone pure cristallise en paillettes jaune pâle.

m-Chlorophényl-p-benzoquinone

La réaction entre le chlorure de diazonium de la *m*-chloraniline (12.8 g.) et la *p*-benzoquinone (13.0 g.) se fait dans 1000 ml. d'eau. Commencée à 15° elle dure 3 heures. On recueille par filtration 21.2 g. de produit pulvérulent jaune. Cristallisée à −10° dans un mélange d'éthanol et d'acétone (2:1), la *m*-chlorophényl-*p*-benzoquinone pure (19.7 g.) est obtenue sous la forme de lamelles jaune pâle.

m-Acétophényl-p-benzoquinone

La réaction du chlorure de diazonium de la *m*-acétophénone (13.5 g.) avec la *p*-benzoquinone (13.0 g.) est commencée à 10° et dure 2 heures. Le produit (21.0 g.) cristallise, après traitement à l'ébullition avec du noir animal dans un mélange d'acétone, de méthanol et d'eau (1:2:1), en aiguilles jaune-orangé.

Méthane sulfonate de la 2-hydroxyphényl-p-benzoquinone

Le méthane sulfonate d'*o*-aminophénol (9.4 g., 0.05 mole) dissous dans un mélange d'acide chlorhydrique concentré (12.5 ml.) et de 50 ml. d'eau est diazoté par une solution de 3.5 g. de nitrite de sodium dans 15 ml. d'eau et versé dans une suspension de 6.5 g. de *p*-benzoquinone dans 425 ml. d'eau à 10° et 15.3 g. d'acétate de sodium hydraté. Après cristallisation du produit de la réaction dans l'éthanol, on récupère 10.7 g. de méthane sulfonate de la 2-hydroxyphényl-*p*-benzoquinone sous la forme d'aiguilles jaune pâle.

o-Tolyl-p-benzoquinone

Un mélange de *o*-toluidine (10.7 g.) diazotée et de *p*-benzoquinone (13.0 g.) réagit pendant plusieurs heures. On isole ensuite le produit cristallin brunâtre (15.4 g.) et on l'extrait à l'éther de pétrole (p.é. 65°–110°) bouillant. Après l'évaporation à sec des extraits éthérés sous pression réduite, on dissout le résidu à chaud dans un mélange de méthanol, d'acétone et d'eau (1:1:1), on bout en présence de noir animal et on obtient, après filtration et refroidissement de la solution à −10°, 12.3 g. d'*o*-tolyl-*p*-benzoquinone cristallisée sous la forme de paillettes jaunes.

o-Anisyl-p-benzoquinone

Le chlorure de diazonium de l'*o*-anisidine (12.3 g.) met 3 heures à réagir avec la *p*-benzoquinone (13.0 g.). Le produit visqueux, que l'on obtient, est extrait à l'éther de pétrole

(p.é. 65°–110°) bouillant. Les extraits réunis sont évaporés à sec sous vide et le résidu est repris à l'ébullition avec du noir animal dans un mélange d'acétone, de méthanol et d'eau (1:1:1). Après cristallisation à -10°, on récupère 17.4 g. d'*o*-méthoxyphényl-*p*-benzoquinone pure sous forme d'un mélange polymorphe d'aiguilles jaune-orangé, p.f. 58°–59°, et de lamelles rouges, p.f. 64°–65°.

o-Diphényl-p-benzoquinone

Le produit brut (25 g., 96%) résultant de l'action du chlorure de diazonium de l'*o*-aminodiphényle (16.9 g.) sur la *p*-benzoquinone (13.0 g.) est isolé après 3 heures de réaction sous la forme d'une poudre jaune amorphe. On le purifie en bouillant à reflux sa solution dans l'acide acétique à 80% avec du noir animal. L'*o*-diphényl-*p*-benzoquinone pure (22.8 g.) cristallise en lamelles jaunes.

o-Chlorophényl-p-benzoquinone

Il faut agiter mécaniquement pendant 5 heures pour que la réaction entre le chlorure de diazonium de l'*o*-chloraniline (12.8 g.) et la *p*-benzoquinone (13.0 g.) se complète. Le dégagement gazeux terminé, on isole 21.1 g. de produit cristallin légèrement brunâtre. On peut le purifier selon l'une ou l'autre des façons suivantes:

Méthode A.—On extrait le produit brut jusqu'à épuisement avec plusieurs portions d'éther de pétrole (p.é. 65°–110°) bouillant et on évapore à siccité sous pression réduite les extraits réunis. On fait bouillir à reflux le résidu avec du noir animal dans un mélange de méthanol, d'acétone et d'eau (1:1:1). Après avoir éliminé le noir animal, la substance pure cristallise dans le mélange de solvants refroidi. On en récupère ainsi 18.1 g.

Méthode B.—On peut également cristalliser le résidu deux fois dans le même mélange de solvants en bouillant chaque fois la solution à reflux avec du noir animal. Le rendement de l'*o*-chlorophényl-*p*-benzoquinone pure cristallisée en paillettes jaunes est alors de 17.2 g.

o-Bromophényl-p-benzoquinone

La réaction du chlorure de diazonium de l'*o*-bromaniline (17.2 g.) avec la *p*-benzoquinone (13.0 g.) dure 6 heures. Le précipité jaune-orangé obtenu pèse 25.6 g. On le cristallise deux fois dans un mélange de méthanol, d'acétone et d'eau (1:1:1) en ayant soin chaque fois de faire bouillir la solution à reflux avec du noir animal. L'*o*-bromophényl-*p*-benzoquinone cristallise en lamelles jaunes.

o-Carbométhoxyphényl-p-benzoquinone

On fait réagir pendant 3 heures le chlorure de diazonium de l'anthranilate de méthyle (15.1 g.) et la *p*-benzoquinone (13.0 g.). Le produit brut filtré et séché pèse 22.2 g. On le cristallise à $-10°$ dans un mélange de méthanol, d'acétone et d'eau (1:1:1) (noir animal). L'*o*-carbométhoxyphényl-*p*-benzoquinone pure (19.5 g.) s'obtient sous forme d'aiguilles jaunes.

o-Nitrophényl-p-benzoquinone

On triture 13.8 g. d'*o*-nitraniline dans 25 ml. d'acide chlorhydrique concentré jusqu'à l'obtention d'une pâte homogène; on étend alors de 100 ml. d'eau et on diazote de la façon habituelle. On fait réagir avec 13.0 g. de *p*-benzophénone. On essore 21.6 g. de produit cristallin. La quinone est isolée en faisant plusieurs extractions successives à l'éther de pétrole (p.é. 90°–110°) bouillant. Les extraits réunis sont évaporés à sec et le résidu cristallisé dans un mélange d'acétone, de méthanol et d'eau (1:2:1) (noir animal). L'*o*-nitrophényl-*p*-benzoquinone pure (17.3 g.) s'obtient en lamelles jaunes.

2,6-Diméthyl-4-bromophényl-p-benzoquinone (16)

On essore 26.8 g. du produit brut de la réaction du chlorure de diazonium de la 2,6-diméthyl-4-bromaniline (20.0 g.) et de la *p*-benzoquinone (13.0 g.) On l'extrait à l'éther de pétrole (p.é. 65°–110°) bouillant. Après l'évaporation à sec des extraits sous pression réduite, le résidu est cristallisé dans un mélange d'acétone, de méthanol et d'eau (1:2:1), après traitement au noir animal. On obtient ainsi 24.1 g. de 2,6-diméthyl-4-bromophényl-*p*-benzoquinone pure sous la forme de paillettes jaunes.

2,6-Dichlorophényl-p-benzoquinone

On obtient de la réaction du chlorure de diazonium de la 2,6-dichloraniline (16.2 g.) et de la *p*-benzoquinone (13.0 g.) 22.7 g. de produit que l'on purifie en extrayant à plusieurs reprises à l'éther de pétrole (p.é. 65°–110°) bouillant, en chassant le solvant des extraits et en cristallisant le résidu dans un mélange d'acétone, de méthanol et d'eau (1:1:1) (noir animal). La 2,6-dichlorophényl-*p*-benzoquinone pure (18.5 g.) cristallise à −10° en lamelles jaunes.

α-Naphtyl-p-benzoquinone

Une suspension d'α-naphtylamine (14.3 g.) dans 300 ml. d'eau est traitée par 16.7 ml. d'acide sulfurique concentré et diazotée de la façon habituelle par 7.0 g. de nitrite de sodium dans 50 ml. d'eau. On verse ensuite cette solution dans une suspension de 13.0 g. de *p*-benzoquinone et de 30.6 g. d'acétate de sodium hydraté dans 650 ml. d'eau à 10°. On agite mécaniquement et on maintient le pH à 5 pendant toute la durée de l'expérience en ajoutant régulièrement de l'acétate de sodium en petites portions. La température s'élève lentement et l'on prend soin de la maintenir inférieure à 20° par l'addition de glace. Après plusieurs heures, on obtient une substance visqueuse qui, après la décantation de la liqueur, est séchée et extraite à la ligroine (p.é. 90°–120°) bouillante. Les extraits refroidis sont de nouveau portés à l'ébullition et décantés. On répète ce procédé jusqu'à ce qu'il ne précipite plus, à la température ordinaire, de goudrons qui restent insolubles à chaud. Les extraits sont alors évaporés à sec sous pression réduite et le résidu est cristallisé dans le méthanol. L'α-naphtyl-*p*-benzoquinone pure (12.3 g.) est obtenue en aiguilles rouges.

REMERCIEMENTS

Nous remercions le Conseil National de Recherches du Canada et la Shell Oil Company of Canada pour des bourses d'étude qu'ils ont accordées à l'un de nous (P.B.).

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L'ARYLATION DES QUINONES PAR LES SELS DE DIAZONIUM

II. SUR LA SYNTHÈSE DES 2,5-BISARYL-*p*-BENZOQUINONES[1]

P. BRASSARD[2] ET P. L'ÉCUYER

RÉSUMÉ

Nous avons réussi la synthèse des 2,5-bisaryl-*p*-benzoquinones en faisant réagir des sels de diazonium avec des monoaryl-*p*-benzoquinones. Cette réaction donne des rendements fort convenables et elle constitue une méthode générale pour la préparation de cette classe de composés, quand elle est exécutée dans des conditions bien déterminées.

INTRODUCTION

Il n'existe à date aucune méthode générale de synthèse (1, 2, 3, 4, 5, 6, 7, 8, 9, 10) des 2,5-bisphénylquinones substituées dans les groupements phényles. Quoique Kvalnes (11) ait constaté qu'il n'est possible de les obtenir qu'avec de très faibles rendements et contaminées par de fortes proportions de dérivé tétrasubstitué par l'action des sels de diazonium sur la benzoquinone, il nous a semblé que la réaction de ces sels avec les monophénylquinones dans des conditions appropriées devrait pouvoir servir de méthode générale pour leur synthèse.

C'est le cas, si on opère dans un milieu qui favorise la précipitation de la 2,5-bisphénylquinone aussitôt formée et l'empêche ainsi de réagir à son tour avec le sel de diazonium. La benzoquinone réagit facilement avec les sels de diazonium en milieux aqueux (12, 13) pour donner des monophénylquinones. Celles-ci sont cependant, en général, trop insolubles dans l'eau pour réagir dans les mêmes conditions, mais elles le font dans un mélange d'un solvant organique et d'eau. L'acide acétique dilué ou l'acétone aqueux s'est révélé, selon le cas, le milieu le plus propice à l'introduction d'un deuxième résidu phényle dans la quinone.

Lorsque la phénylquinone de départ est très soluble dans les solvants organiques, il est préférable d'employer le mélange eau – acide acétique pour éviter la formation du dérivé tétrasubstitué. Par contre, avec une phénylquinone moins soluble le mélange eau–acétone donne de meilleurs résultats. Il faut toutefois dans cette dernière alternative opérer à une température inférieure à 0°.

Nous n'avons constaté aucun avantage à employer des sels cuivriques (chlorure ou acétate) comme catalyseur de la réaction. Ceci est d'autant plus surprenant que d'après Marini-Bettòlo et Rossi (14) l'addition de poudre de bronze améliore le rendement de l'arylation de la 1,4-naphtoquinone en milieu acétique.

Nous avons vérifié la généralité de cette méthode de synthèse des 2,5-bisphénylbenzoquinones en en préparant plusieurs à partir de sels de diazonium représentant toute la gamme de réactivité (Tableau I).

PARTIE EXPÉRIMENTALE

On diazote entre 0° et 5° l'amine (0.05 mole) dissoute dans un mélange de 25 ml. d'eau et de 12.5 ml. d'acide chlorhydrique concentré en ajoutant lentement une solution de 3.5 g. de nitrite de sodium dans 15 ml. d'eau. La solution du sel de diazonium est ensuite versée dans un mélange de la phénylquinone (0.045 mole), de 20.4 g. (0.15 mole)

[1]*Manuscrit reçu le 23 décembre 1957.*
Contribution du Département de Chimie de la Faculté des Sciences, Université Laval, Québec, Qué. Ce mémoire est tiré de la thèse de doctorat de P. Brassard.
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TABLEAU I

2,5-BISARYL-*p*-BENZOQUINONES

p-Benzoquinone	P.f.,°*	Rdt., %	Solvant	Forme cristalline	Formule	Analyse	
						% calculé	% trouvé
2-Phényl-5-(*p*-anisyl)-	170–171	32	Ethanol–acétone (2:1)	Paillettes jaunes	$C_{19}H_{14}O_3$		
2-Phényl-5-(*m*-bromophényl)-	207–208	32	Butanol	Aiguilles orangées	$C_{18}H_{11}O_2Br$	C, 63.73 H, 3.27	C, 63.9 H, 3.3
2,5-Bis-(*m*-chlorophényl)-	Subl.	46	Acide acétique	Lamelles orangées	$C_{18}H_{10}O_2Cl$	C, 65.67 H, 3.06	C, 65.9 H, 3.6
2-Phényl-5-(*o*-anisyl)-	161–162	20	Ethanol-acétone (2:1)	Aiguilles orangées	$C_{19}H_{14}O_3$	C, 78.60 H, 4.86	C, 78.5 H, 5.0
2,5-Bis-(*p*-chlorophényl)-	Subl.	43	Toluène ou acide acétique	Aiguilles rouges	$C_{18}H_{10}O_2Cl_2$	C, 65.67	C, 65.9
2,5-Bis-(*o*-chlorophényl)-	194–196	42	Méthanol–acétone (4:1)	Aiguilles jaunes	$C_{18}H_{10}O_2Cl_2$	H, 3.06 C, 65.67 H, 3.06	H, 3.3 C, 65.3 H, 3.2
2,5-Bis-(*o*-bromophényl)-	217–219	40	Ethanol–butanone (2:1)	Aiguilles jaunes	$C_{18}H_{10}O_2Br_2$	C, 51.71 H, 2.41	C, 51.6 H, 2.5
2,5-Bis-(*o*-carbométhoxyphényl)-	187–188	38	Ethanol–acétone (2:1)	Lamelles jaunes	$C_{20}H_{15}O_6$		
2,5-Bis-(*o*-nitrophényl)-	208–210	50	Butanol–acétone (1:2)	Lamelles jaunes	$C_{18}H_{10}O_6N_2$	C, 61.72 H, 2.88 N, 8.00	C, 61.6 H, 2.9 N, 8.2
2-Phényl-5-(β-naphtyl)-	214	36	Butanol	Aiguilles orangées	$C_{22}H_{14}O_2$	C, 85.14 H, 4.56	C, 85.2 H, 4.5

**Les points de fusion ont été pris à l'aide de l'appareil de Johns.*

d'acétate de sodium trihydraté et de 200 à 250 ml. d'acide acétique agité mécaniquement. On ajoute alors suffisamment d'eau (environ 75 à 100 ml.) pour produire une légère précipitation de la quinone de départ. Tout en maintenant l'agitation du milieu, on peut laisser réagir à la température ambiante ou, s'il le faut, on chauffe très légèrement le mélange jusqu'à l'obtention d'un dégagement modéré d'azote sans toutefois dépasser une température de 40° à 45°.

Une fois le dégagement gazeux terminé, on étend d'eau, on isole le précipité et on le dissout dans un mélange d'acétone et de méthanol (1:4) bouillant. On laisse cristalliser la quinone en abandonnant la solution pendant quelques jours au réfrigérateur à −10°. En diluant les eaux-mères de cristallisation avec un peu de méthanol et en les laissant séjourner au réfrigérateur on augmente le rendement d'une façon appréciable. La 2,5-bisphénylquinone est obtenue presque pure. Si nécessaire, on peut la purifier davantage en la recristallisant dans les solvants appropriés.

Quand la phénylquinone de départ n'est pas assez soluble dans l'acide acétique ou lorsque le sel de diazonium l'exige, ce qui est le cas, par exemple, pour la *m*-chlorophénylquinone et le sel de diazonium de la β-naphtylamine, on dissout la phénylquinone dans l'acétone (300 ml. pour 0.045 mole), on refroidit la solution à −5° et on y verse la solution du sel de diazonium. Tout en agitant mécaniquement et en maintenant la température à −5°, on introduit l'acétate de sodium trihydraté (20.4 g. en tout) en petites portions durant une période de 20 minutes. On laisse ensuite le mélange se réchauffer à la température ambiante. L'isolement de la quinone se fait comme précédemment.

REMERCIEMENTS

Nous remercions le Conseil National de Recherches du Canada et la Shell Oil Company of Canada pour des bourses d'études qu'ils ont accordées à l'un de nous (P.B.).

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REACTIVITY STUDIES ON NATURAL PRODUCTS

IV. DISSOCIATION CONSTANTS OF THE CYANOHYDRINS OF SOME STEROID KETONES[1]

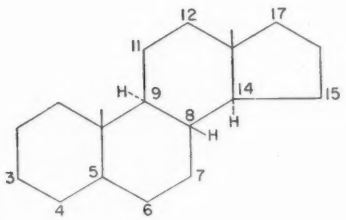
OWEN H. WHEELER[2] AND JOSÉ L. MATEOS[3]

ABSTRACT

The dissociation constants of the cyanohydrins of 3-, 6-, and 7-ketocholestane, 3-keto-coprostane, Δ^4- and Δ^5-cholestenone, and Δ^7-, $\Delta^{8(9)}$-, $\Delta^{8(14)}$-, and Δ^{14}-ergosten-3-one have been measured in 80% dioxane at 25.0°. Cholestan-3-one and coprostan-3-one have essentially the same reactivity. 6- and 7-Ketocholestane show "eclipsing" effects of neighboring hydrogen atoms. Δ^4- and Δ^5-Cholestenone are less reactive than cholestanone owing to the electronic effect of the double bond, but Δ^7-, $\Delta^{8(9)}$-, $\Delta^{8(14)}$-, and Δ^{14}-ergostenone are more reactive, the effect decreasing with the distance of the double bond from the 3-keto group.

INTRODUCTION

While quantitative studies have been made on the reactivity of steroid esters and alcohols (1, 2), few quantitative data have been published on the relative reactivity towards addition reactions of a keto group in various positions of the steroid molecule, the only work of this nature being studies of the rates of oxime formation of 3-, 4-, 6-, and 7-ketocholestane (3), and of the borohydride reduction of 3- and 20-ketopregnanone (4). It is known that certain postions, e.g., 11 and 12, are unreactive with respect to a 3-keto group, but no systematic study has been made of the reactivity of groups in rings A and B, where reactivity differences would be expected to be small. The determination of ketone–cyanohydrin equilibria provides a convenient method of studying ketone reactivity towards addition reactions (5), and the dissociation constants of the cyanohydrins of 3-keto-cholestane and -coprostane (rings A/B *trans* and *cis*, respectively), 6- and 7-keto-cholestane, and 3-keto steroids with double bonds in positions 4,5,7,8(9),8(14), and 14 have been measured in 80% dioxane–water at 25.0° (see Table I), to investigate the influence of substitution in various positions, of *cis–trans* ring A/B fusion, and the effect of double bonds.



Cholestan-3-one and coprostan-3-one differ only in the nature of the ring A/B fusion. The *trans* fusion in the former case gives the molecule a continuous zigzag form, whereas the *cis* fusion, in the latter, leads to an L-shaped structure (6, 7). In cholestane the methyl group at C-10 and the 9—10 bond are *axial and equatorial* respectively (with respect to ring A), and in the second case are reversed, but in both cases the hydrogen atom at

[1]*Manuscript received November 25, 1957.*
Contribution from the Instituto de Quimica, Universidad Nacional Autonoma de Mexico, Mexico, 20, D.F. Part III, Chemistry and Industry, 395 (1957).
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TABLE I

DISSOCIATION CONSTANTS OF CYANOHYDRINS[a]

	$K \times 10^2$	Ratio[b]
Cyclopentanone	56.0±1.0	9.3
Cyclohexanone	6.00±0.10	1.0
Cholestan-3-one	5.42±0.05	0.90
Coprostan-3-one	5.97±0.09	1.0
Cholestan-6-one	7.22±0.13	1.2
Cholestan-7-one	1.25±0.01	0.21
Δ^4-Cholesten-3-one	38.4±0.60	6.4
Δ^5-Cholesten-3-one	7.94±0.15	1.3
Δ^7-Ergosten-3-one	4.09±0.14	0.68
$\Delta^{8(9)}$-Ergosten-3-one	3.97±0.12	0.66
$\Delta^{8(14)}$-Ergosten-3-one	4.50±0.02	0.75
Δ^{14}-Ergosten-3-one	5.43±0.02	0.90

[a] *In 80% dioxane at 25.0°±0.1°.*
[b] *Ratio of dissociation constant to cyclohexanone = 1.0.*

C-5, one carbon atom nearer, is axial and the 5—6 bond equatorial and thus no large steric effect to cyanohydrin formation due to "axial crowding" (5) would be expected, and both these ketones have essentially the same cyanohydrin dissociation constant as cyclohexanone. The small increased reactivity of cholestanone with respect to cyclohexanone may be due to an "equatorial crowding" effect (5) similar to that observed in alkyl cyclohexanones, whereby the large internal carbonyl angle of the ketone distorts both rings A and B. The distortion is relieved in forming an addition product and addition is, therefore, facilitated.

6- and 7-Ketocholestane both have an extra alkyl substituent in the α-position, and this will exert an inductive effect which will increase the dissociation constant (5). However, the 6-ketone shows only a small increase while the 7-ketone actually shows a large decrease in dissociation constant and another effect must be operating. Construction of models shows that in the case of the 7-ketone the steric geometry of the steroid molecule is such that an α-hydrogen atom at C-15 is brought very close to the carbonyl group. Addition to the keto group gives a staggered structure and reduces the unfavorable oxygen–hydrogen interactions and is thus favored (8). This shielding or "eclipsing" effect has previously been observed to affect the stabilities of α-decalone and the 1,4-keto-perhydrophenanthrenes (9). In the case of the 6-ketone the small "eclipsing" effect of the hydrogen atoms on C-4 will tend to increase the extent of cyanohydrin formation, but there will be an "axial crowding" effect (5) in the cyanohydrin, between the methyl group at C-10 (2) and the cyanide (or hydroxyl) group. The net result of these opposing effects is a small decrease in reactivity, with respect to cholestan-3-one.

Δ^4- and Δ^5-Cholestan-3-one are both less reactive towards cyanohydrin formation than 3-cholestanone. In the former case, addition to the ketone grouping will destroy the resonance conjugation of the α,β-unsaturated ketone system and hence cyanohydrin formation will be difficult. (Whether addition was 1,4 as well as 1,2 was not determined. However, the reaction was unimolecular in ketone and cyanide.) The decreased reactivity of Δ^4-3-keto steriods, as compared to 3-keto steroids, towards dioxalan formation (10), ketal formation (11), and borohydride reduction (12) has previously been noted. In the Δ^5-compound there will be an inductive (or hyperconjugative) donation of electrons by the double bond to the ketone group (analogous to double-bond participation in the solvolysis of cholesteryl-*p*-toluene sulphonate (13)) and this will decrease the polarity of the ketone grouping and reduce nucleophilic attack of cyanide ion.

In contrast to the behavior of the Δ^4- and Δ^5-compounds, the four ergosten-3-ones (Δ^7, $\Delta^{8(9)}$, $\Delta^{8(14)}$, and $\Delta^{(14)}$) show increased reactivity but in an order decreasing with distance of the double bond from the ketone grouping, until no effect is apparent in the Δ^{14}-compound. This effect is probably not electronic, since the double bonds are too far removed from the keto group, and though the Δ^4- and Δ^5-ketones show displacements of ketone absorption in both the ultraviolet and the infrared (see Table II) due to electronic effects, the ergostenones are no different from cholestanone.

TABLE II

ABSORPTION SPECTRA OF KETONES

	I. R., cm.$^{-1}$	U. V.,[c] mμ
Cholestan-3-one	1716[a]	280 (73)
Coprostan-3-one	1714[a]	280 (73)
Δ^4-Cholesten-3-one	1627, 1675[a]	240.5 (18,000)[d]
		312 (100)
Δ^5-Cholesten-3-one	1683, 1724[a]	285 (100)
Δ^7-Ergosten-3-one	1712[b]	280 (59)
$\Delta^{8(9)}$-Ergosten-3-one	1715[b]	280 (57)
$\Delta^{8(14)}$-Ergosten-3-one	1718[b]	280 (56)
Δ^{14}-Ergosten-3-one	1715[b]	280 (62)

[a]*In carbon tetrachloride solution. K. Dobriner, E. R. Katzenellenbogen, and R. N. Jones. Infrared absorption spectra of steroids—An atlas. Interscience Publishers, Inc., New York, N.Y. 1953.*

[b]*Present work, as nujol mulls.*

[c]*As ethanolic solutions. Present work, unless otherwise stated.*

[d]*Ref. 40.*

Cyclohexene exists in a preferred "half-chair" conformation (14, 15), in which all the angles are slightly distorted (16), and introduction of a double bond into the steroid nucleus will lead to an over-all flattening of the rings. This will slightly distort ring A and introduce small non-bonded interactions. Cyclohexanone, itself, is a slightly distorted structure and its reactivity is due partly to the tendency to form an undistorted addition product (8). The presence of a keto group in ring A will introduce non-bonded interactions in this ring, and these will be increased by the conformational distortions produced by a double bond in a neighboring ring. Thus addition to the keto group, which will partially relieve the unfavorable interactions, will take place more readily than in the case of the saturated ketones. The effect of Δ^7 and $\Delta^{8(9)}$ double bonds, which are on either side of the C-3 to C-8 axis of rings A and B, is the same. A $\Delta^{8(14)}$ double bond, which is exocyclic to these two rings, has less effect and a Δ^{14} double bond, one more carbon atom remote and in another ring, has no measurable effect. Barton and co-workers (17, 18) have recently shown the operation of long-range effects in the mutarotation of steroid 5,6-dibromides and in the condensation of 3-keto triterpenes with benzaldehyde and has introduced the term "conformational transmission" for the transmission of distortions through a molecule by flexing of valency angles and alteration of atomic co-ordinates. Since no electronic interactions are involved and the effect is purely a steric one, it will manifest itself in an entropy term, and Barton and Head observed no difference in the energy of activation for the dibromides studied, but found small differences in the frequency factor. In the present work the maximum difference, between $\Delta^{8(9)}$-ergosten-3-one and cholestan-3-one, corresponds to a free-energy difference of only 0.18 kcal.

The ketones were generally prepared by standard methods (see Experimental), but in the course of the work some interesting observations were made. Ergosteryl acetate is

hydrogenated in ethyl acetate under ordinary conditions to Δ^7-ergostenyl acetate, but with Raney nickel at high temperature and pressure the product formed was $\Delta^{8(14)}$-ergostenyl acetate. This isomerization has previously been noted with platinum oxide in acetic acid (19). As an alternative to oxidation with chromium trioxide in acetic acid and benzene (20), or Oppenauer oxidation (21), the oxidation of some of the unsaturated alcohols with chromium trioxide in pyridine (the Sarett reagent (22)) was investigated. Cholesterol itself gave a mixture consisting largely of Δ^4-cholestenone but oxidation of Δ^7-ergostenol proceeded without rearrangement. This reagent has been recently used for the oxidation of ursa-9(11),12-dien-3-ol (23) without rearrangement of the double bond. However, it was found that use of only a small excess of chromium trioxide in acetic acid and benzene gave better yields, and this method was generally employed. The isomerization of $\Delta^{8(14)}$-ergostenone to Δ^{14}-ergostenone with hydrogen chloride in chloroform (24, 25) proved to be incomplete (26, 27). Various conditions of time and temperature were tried but the best yield obtained was only a 20% conversion. The isomerization of the corresponding acetate or alcohol gave poorer yields.

EXPERIMENTAL

Ketones

Cyclopentanone and cyclohexanone were specimens which had been previously prepared in this laboratory (5).

Cholestanone, m.p. 129°–130°, was prepared by oxidation of cholestanol (28), and coprostanone, m.p. 61°–63°, $(\alpha)_D$ +36°, by reduction of cholestenone (21) over a palladium charcoal catalyst in ethyl acetate, with the addition of two drops of piperidine. Δ^5-Cholestenone was prepared by the oxidation and subsequent zinc-dust reduction of cholesterol dibromide (29).

Cholestan-6-one

Cholesterol was converted to cholesteryl bromide, m.p. 97°–98°, $(\alpha)_D$ −20° (lit. m.p. 97°–99°, $(\alpha)_D$ −21.6° (30)), with phosphorus tribromide in benzene (31) and the bromide nitrated with fuming nitric acid and sodium nitrite to 3-bromo-6-nitrocholest-5-ene, m.p. 153°–155°, λ_{max} 262 mμ, ϵ 2200. Zinc-dust reduction (32) gave the required ketone.

Cholestan-7-one

Cholesteryl acetate was oxidized with *t*-butyl chromate (33) to 7-ketocholesteryl acetate, m.p. 157°–160°, $(\alpha)_D$ −86°, which was converted by refluxing with concentrated hydrochloric acid to $\Delta^{3,5}$-cholestadien-7-one, m.p. 112°–113° (lit. m.p. 112° (34)). Reduction of this compound with platinum oxide in ethyl acetate gave the required ketone, m.p. 116°–118°, $(\alpha)_D$ −28°, λ_{max} 292 mμ, ϵ 70 (lit. m.p. 116°–118° (35)).

Δ^7-*Ergosten-3-one*

Hydrogenation of ergosterol in ethyl acetate and ether at 30 lb. pressure with a platinum oxide catalyst gave Δ^7-ergosten-3-ol. Oxidation by the method of Oppenauer, with chromium trioxide (1.2 equiv.) in acetic acid and benzene, or by the method of Sarett, gave the ketone, m.p. 159°–160°, $(\alpha)_D$ +22° (lit. m.p. 159°, $(\alpha)_D$ +22° (36)), in about 50% yield in each case. Hydrogenation of ergosteryl acetate in ethyl acetate and acetic acid at 30 lb. pressure with a 5% palladium–charcoal catalyst, or in ethyl acetate at 1000 lb. pressure and 100° using a Raney nickel catalyst, gave $\Delta^{8(14)}$-ergostenyl acetate.

$\Delta^{8(14)}$-*Ergosten-3-one*

Oxidation of $\Delta^{8(14)}$-ergostenol with chromium trioxide in acetic acid and benzene gave

the ketone, m.p. 128°–129°, $(\alpha)_D$ +31.5° (lit. m.p. 129°–130°, $(\alpha)_D$ +30° (36)), in 70% yield. Oppenauer oxidation gave a 50% yield.

$\Delta^{8(9)}$-Ergosten-3-one

This was prepared by oxidation of $\Delta^{8(9)}$-ergostenol (37) with chromium trioxide in benzene and acetic acid, and had m.p. 118°–120°, $(\alpha)_D$ +70°.

Δ^{14}-Ergosten-3-one

This was prepared by isomerization of $\Delta^{8(14)}$-ergosten-3-one with hydrogen chloride in chloroform. The method gave only partial conversion, but the two isomers could be separated by careful chromatography on neutral alumina using hexane as eluent. The highest conversion (20%) was obtained by saturating with hydrogen chloride at 0° and allowing to stand 3–4 days in a refrigerator at *ca.* 5°. Poorer conversions were obtained with the alcohol or acetate. The pure ketone had m.p. 149°–150°, $(\alpha)_D$ +40° (lit. m.p. 149°–151°, $(\alpha)_D^{20}$ +36.4° (26)).

Solvents

Dioxane (Matheson, Coleman, and Bell) was refluxed with potassium hydroxide and fractionated from a fresh quantity. This dioxane (80 vol.) was mixed with distilled water (20 vol.), and the resulting solvent had d_4^{25} 1.0345.

Cyanohydrin Formation

Some preliminary experiments were carried out to find a suitable solvent. The steroids were not sufficiently soluble in ethanol. The dissociation constants of the cyanohydrin of cyclopentanone in anhydrous dioxane and 95% dioxane at 25° were *ca.* 700×10^{-2} and 200×10^{-2} respectively. Accordingly 80% dioxane was chosen as a solvent in which the steroids were reasonably soluble and which gave convenient dissociation constants. The procedure adopted was to dissolve the ketone (0.2–0.4 g.) in 80% dioxane in a 100 ml. graduated flask and then to add a solution of hydrogen cyanide (10 ml. of *ca.* 0.15 *N*), prepared from sodium cyanide and sulphuric acid and dissolved in 80% dioxane. A catalyst solution (1 ml.) of 2% tri-*n*-propylamine in 80% dioxane was added and the flask made up to the mark and allowed to equilibrate in a bath at 25.0°±0.1° for 6 hours. Aliquots (10 ml.) of the solution were withdrawn, added to excess silver nitrate (*ca.* 0.1 *N*) containing 0.5% nitric acid, and the excess silver nitrate titrated with potassium thiocyanate (0.05 *N*), using ferric ammonium sulphate as indicator (38, 39). Each experiment was repeated three or more times and the results, together with their mean standard deviations, are given in Table I.

ACKNOWLEDGMENTS

The authors are grateful to the Rockefeller Foundation, New York, for financial assistance.

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NOTES

THE DETERMINATION IN SITU OF THE CARBON CONTENT OF SOLID PRODUCTS IN REACTION VESSELS[1]

A. W. TICKNER

During an investigation of the reactions of methane in an electric discharge it was found that part of the methane was converted to a solid product which appeared as a thin film on the electrodes and, to a lesser extent, on the walls of the discharge tube. Enough of the solid was obtained by running for a long period at relatively high discharge currents to show that the composition was, very approximately, $(C_2H_3)_n$. Since the total weight of the deposit was usually of the order of 0.1 mg. and it was distributed over an area of between 10 and 100 cm.^{2} on surfaces which were not readily accessible, it was difficult to determine the total amount of carbon in the deposit by any of the standard procedures. The procedure described in this note was worked out in an effort to estimate the total carbon content of the solid product and thus to complete the material balance for the discharge reaction.

The discharge tube used was made of Pyrex tubing 4.0 cm. in diameter and was so designed that it could be surrounded by liquid nitrogen during an experiment. The electrodes were stainless steel disks 3.5 cm. in diameter mounted 3.0 cm. apart. Since direct current was used, this arrangement had the effect, at the pressures employed, of restricting the discharge to the negative glow. The total volume of the discharge system was approximately 500 cm.^{3}

After a discharge experiment with methane, the volatile products were removed, leaving the solid deposit on the electrodes and walls of the discharge tube. The discharge tube was then immersed in liquid nitrogen, and oxygen was introduced to a pressure of about 1 mm. of mercury. The discharge was turned on and run at a current of about 10 ma. until the oxygen pressure had fallen to a constant value. This constant value, which was usually about 0.3 or 0.4 mm. below the initial pressure, was attained in a few minutes and coincided with the disappearance of the last visible traces of the deposit from the cathode, where it had been deposited most heavily. The discharge was then turned off and the remaining oxygen pumped away.

Following the removal of the oxygen the discharge tube was warmed to the temperature of dry ice. This temperature was chosen in order to retain any water formed. The gas evolved was removed with a Toepler pump and its volume measured. Analysis on a mass spectrometer showed that the gas consisted of carbon dioxide and a small amount of oxygen. On the assumption that all of the carbon in the deposit had been converted into carbon dioxide, it was then possible to calculate the carbon content of the solid product obtained in the discharge reaction.

In order to test the method, a number of determinations were made using deposits consisting of measured amounts of materials of known carbon content. Each substance was made into a solution (in the case of graphite, a suspension) of known concentration, and a measured volume was evaporated on the surface of the cathode. It was estimated that the weight of a deposit produced in this way was known to within $\pm 2\%$. The

[1]*Issued as N.R.C. No. 4652.*

cathode was inserted into the discharge tube, which was evacuated and surrounded with liquid nitrogen. The deposit was then oxidized with the oxygen discharge and the products were measured and analyzed as described in the preceding paragraph.

The substances used were chosen to represent different types of compounds. All of them were required to have low volatility since the discharge tube had to be thoroughly evacuated before each experiment. The graphite used was Acheson Colloids Co. "Aquadag". Its graphite content was determined by drying a sample at 180° C. for 24 hours. It was used in the form of a suspension in distilled water. A sample of polyethylene polymer having a molecular weight of about 2500 was obtained and applied to the electrode as a toluene solution. Reagent grade *o*-terphenyl was used in benzene solution and Reagent grade sucrose in water. In addition, a luminous burner flame was used to deposit a thin but clearly visible deposit of carbon black on the cathode. The oxygen used was from a standard cylinder supply having a stated purity of 99.9%. It was passed through a trap cooled by liquid nitrogen and was used without any further purification.

The results of these determinations have been summarized in Table I. In each case the recovery of carbon as carbon dioxide was sufficiently quantitative to meet the present requirements.

TABLE I

RECOVERY OF CARBON AS CARBON DIOXIDE

Sample	Gram atoms of carbon deposited ($\times 10^6$)	Moles of carbon dioxide recovered ($\times 10^6$)	% Theoretical
Graphite	16.9	16.7	99
Polyethylene	12.4	12.0	97
o-Terphenyl	11.7	11.8	101
Sucrose	15.0	14.3	95

In addition, the experimental results showed another, and rather unexpected, correlation. As reported above, the gas recovered after the oxidation of each deposit contained some oxygen in addition to the carbon dioxide. This amount of oxygen could not be decreased even by prolonged pumping with the products of the discharge oxidation frozen out at the temperature of liquid nitrogen. A relationship appeared to exist between the percentage of oxygen in the carbon dioxide recovered and the amount of hydrogen present in the compound which had been oxidized. The values obtained for the various substances used are shown graphically in Fig. 1. On this basis the composition of the solid product formed in the discharge reaction of methane is given approximately by the formula $(CH)_n$.

No detailed explanation is offered to account for the oxygen retained in the discharge product. The 8 or 9% of oxygen found in the products of the discharge oxidation of pure carbon may represent oxygen retained in some way by the solid carbon dioxide or as an unstable carbon–oxygen compound which decomposes on being warmed to −78° C. The remainder of the oxygen, the part which appears to be related to the hydrogen content of the solid being oxidized, may be due to the formation of hydrogen–oxygen compounds which decompose on being warmed above the temperature of liquid nitrogen. Such compounds have been reported by Jones and Winkler (1) and by Giguère, Secco, and Eaton (2) as products of the decomposition of water vapor in the electric discharge.

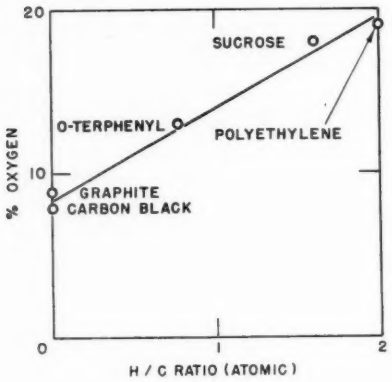

FIG. 1.

The method described above would seem to be capable of fairly wide application to situations in which it is desired to determine the carbon content of small amounts of organic solids deposited in inaccessible locations. While the work reported here has made use of a direct-current discharge in a tube with internal electrodes, it seems likely that an electrodeless discharge using radio-frequency power would also be effective. Furthermore, although the present discharge tube was arranged to allow it to be immersed in liquid nitrogen, it should be possible to carry out the oxidation successfully in a system in which the oxygen is circulated through the discharge and subsequently passed through a cold trap before being returned to the discharge chamber. With these variations it should be possible to apply the method to the determination of carbon in organic deposits in a variety of reaction vessels, including, for example, the reaction cells used in photochemical experiments. In addition, it may be possible to use the method to estimate the hydrogen content of such deposits.

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RECEIVED DECEMBER 9, 1957.
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THE THERMODYNAMIC PROPERTIES OF BENZOIC ACID[1]

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Dr. R. S. Jessup has pointed out to us in a private communication that in a previous note (1) of the same title we have used the wrong value for the standard heat of combustion of benzoic acid to calculate its thermodynamic properties. The value that we used, 26,428.4±2.6 int. j. g.$^{-1}$, should be replaced by 26,420.4±2.6 int. j. g.$^{-1}$. This value has been corrected for the changed atomic weight of carbon (2) by Dr. Jessup to give 3226.99±.31 kj. mole^{-1}. In addition there are numerical errors in our table of entropies,

[1]*Issued as N.R.C. No. 4653.*

and consequently also in the free energies. The entropy relative to that at 0° K. had been calculated by Furukawa, McCoskey, and King (3), in a paper which we had overlooked; our revised values agree with theirs.

Solid benzoic acid at room temperature is composed of molecules of dimer (4) and no thermal transition has been observed between 15° K. and room temperature (3). If the hydrogen bonds in the dimer are completely disordered the zero-point entropy is $\frac{1}{2}R\ln 2$ (5). There is no experimental information on the zero-point entropies of carboxylic acids, but the disordered structure of ice and heavy water is well verified. If the maximum disorder is present in benzoic acid, and this seems likely, 0.347 should be added to $(S-S_0°)/R$ to give the entropy. The entropies thus obtained are given in the revised Table I,

TABLE I

T/° K.	$(H_T°-H_0°)/RT_0$	$S°/R$	$-(F_T°-H_0°)/RT$	$-(\Delta F_f°)/RT$
		Solid		
100	1.544	7.854	3.636	402.95
150	3.160	11.40	5.65	251.37
200	5.202	14.59	7.48	175.11
220	6.146	15.82	8.19	154.24
240	7.165	17.03	8.88	136.80
260	8.264	18.23	9.55	122.03
280	9.442	19.42	10.21	109.32
298.15	10.58	20.50	10.80	99.26
300	10.70	20.61	10.86	98.29
310	11.36	21.20	11.19	93.31
320	12.04	21.78	11.50	88.64
330	12.74	22.38	11.83	84.26
340	13.46	22.97	12.15	80.13
350	14.21	23.56	12.47	76.22
360	14.97	24.14	12.78	72.55
370	15.75	24.73	13.10	69.04
380	16.56	25.31	13.41	65.73
390	17.38	25.91	13.72	62.59
395.52	17.85	26.23	13.90	60.94
		Liquid		
395.52	25.78	31.70	13.90	60.94
400	26.27	32.04	14.10	59.68
410	27.40	32.80	14.54	56.98

herewith. The free energy and the free energy of formation have also been recalculated. The free energy of graphite was obtained by graphical interpolation of the data in Reference 6 below 300° K., and of those in Reference 7 above 300° K.

The revised heat of formation at 0° K. is $-367.75\pm.45$ kj. mole^{-1} and at 25° C. is $-385.16\pm.40$ kj. mole^{-1}. The physical constants used are from References 2 and 8, and 1 mole of benzoic acid refers to the formula $C_7H_6O_2$.

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Received July 17, 1957.
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1-ARYLSULPHONYL-3-*n*-BUTYL-2-METHYL-2-THIOPSEUDOUREAS

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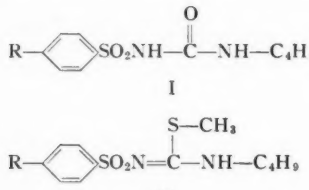
Compounds containing the thiopseudourea grouping have recently come under investigation in our laboratories (1). Since certain 1-arylsulphonyl-3-*n*-butylureas (I) have been shown to possess useful hypoglycemic activity, it was of interest to prepare some 1-arylsulphonyl-3-*n*-butyl-2-methyl-2-thiopseudoureas (II) for pharmacological screening. Cox (2) has reported the preparation of a series of 1-arylsulphonyl-2-methyl-2-thiopseudoureas which have shown some value as bacteriostatic agents.



(*a*) R = CH_3
(*b*) R = $NHCOCH_3$
(*c*) R = NH_2

The sulphonylthiopseudoureas were prepared by the condensation of the appropriate sulphonyl chlorides with 1-*n*-butyl-2-methyl-2-thiopseudourea. Acid hydrolysis of 1-(*p*-acetaminobenzenesulphonyl)-3-*n*-butyl-2-methyl-2-thiopseudourea (II*b*) gave the 1-(*p*-aminobenzenesulphonyl)-3-*n*-butyl-2-methyl-2-thiopseudourea (II*c*).

The sulphonylthiopseudoureas were administered orally to rabbits which had been fasted for 24 hours. None of the compounds tested showed a significant hypoglycemic action.

EXPERIMENTAL*

1-(p-Toluenesulphonyl)-3-n-butyl-2-methyl-2-thiopseudourea

Potassium carbonate (33 g., 0.24 mole) was suspended in 90 ml. of a 3:1 acetone–water solution cooled in an ice-water bath. A well-ground mixture of *p*-toluenesulphonyl-chloride (12.4 g., 0.065 mole) and 1-*n*-butyl-2-methyl-2-thiopseudourea hydroiodide† (19.9 g., 0.0725 mole) was slowly added with vigorous stirring. The addition was completed after 30 minutes and the stirring was continued at room temperature for another 3 hours. The reaction contents were then added to 250 ml. of water, causing the product to separate out, 17.8 g. (91% yield), m.p. 72°–77° C. Two recrystallizations from isopropanol gave 11.5 g., m.p. 85°–86° C. Calculated for $C_{13}H_{20}N_2S_2O_2$: C, 51.97; H, 6.71; N, 9.32; S, 21.35. Found: C, 52.25; H, 6.92; N, 9.19; S, 20.93.

1-(p-Acetaminobenzenesulphonyl)-3-n-butyl-2-methyl-2-thiopseudourea

This compound was prepared in the same manner as the preceding example. Potassium carbonate (66 g., 0.48 mole), *p*-acetaminobenzenesulphonyl chloride (30.3 g., 0.13 mole), and 1-*n*-butyl-2-methyl-2-thiopseudourea hydroiodide† (39.2 g., 0.143 mole) gave 44 g. of product with m.p. 129°–135° C. Two recrystallizations from isopropanol gave 21.8 g., m.p. 141°–142° C. Calculated for $C_{14}H_{21}N_3S_2O_2$: C, 48.96; H, 6.17; N, 12.24; S, 18.67. Found: C, 49.15; H, 6.02; N, 12.11; S, 18.51.

**All melting points are uncorrected.*
†*The preparation of this compound is described by Kirsten and Smith (3).*

1-(p-Aminobenzenesulphonyl)-3-n-butyl-2-methyl-2-thiopseudourea

1-(*p*-Acetaminobenzenesulphonyl)-3-*n*-butyl-2-methyl-2-thiopseudourea (15.5 g., 0.045 mole) was refluxed for 2 hours in a solution consisting of 67 ml. of 7% hydrochloric acid and 30 ml. of ethanol. After cooling and addition of a large amount of water, the solution was neutralized with ammonium hydroxide, causing the product to separate out, 12.8 g. (95% yield), m.p. 158°–159° C. One recrystallization from methanol did not raise the melting point. Calculated for $C_{12}H_{19}N_3S_2O_2$: C, 47.81; H, 6.35; N, 13.94; S, 21.28. Found: C, 48.35; H, 6.72; N, 14.06; S, 21.10.

ACKNOWLEDGMENTS

The authors are grateful to Mr. W. J. Turnbull for the microanalytical data and to Dr. C. I. Chappel for the pharmacological screening.

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RECEIVED DECEMBER 18, 1957.
RESEARCH AND BIOLOGICAL LABORATORIES,
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MONTREAL, QUE.

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